# LABORATORY MANUAL OF ELEMENTARY COLLOID CHEMISTRY

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BY

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# PREFACE.

Although most of the existing text-books of Colloid Chemistry necessarily give, in more or less detail, descriptions of experimental procedure and instructions for making many of the classical preparations, no laboratory manual or collection of practical exercises such as has been found indispensable in the teaching of other branches of chemistry has so far appeared. The lack of such a work is all the more likely to check the spread of a practical knowledge of the discipline, as many of the methods and materials of colloid chemistry are peculiar, and strange even to students well trained in inorganic and organic chemistry.

The present work is an attempt to fill this gap and to supply accurate and very detailed directions for carrying out the fundamental operations, for making a number of representative preparations, and for examining them by the standard methods. These are based throughout on personal experience of the processes described and of the difficulties experienced in teaching them. The examples chosen are, generally speaking, the simplest ones and, where alternatives are possible, those involving the smallest expenditure in apparatus and material. The task of selection has not been easy, and the attempt to delimit the elementary region of the whole domain may seem premature or arbitrary: the guiding principle has been to provide for the wants of those students of numerous branches of science who are finding some training in colloid chemistry an indispensable part of their equipment, and are able to devote a limited time only to acquiring its technique.

For the guidance of readers desirous of going beyond the limits of this manual a number of references to recent literature are given at the end of each section. The papers quoted are mostly records of experimental investigations which are either alternative to, or more advanced than, the examples given in the text.

Since the book is the first of its kind, the author will be very grateful for hints from readers who may find any of the directions given in it lacking in clearness or capable of being simplified.

EMIL HATSCHEK.

London,
*February*, 1920.

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# A LABORATORY MANUAL OF ELEMENTARY COLLOID CHEMISTRY.

## CHAPTER I.

## GENERAL REMARKS ON APPARATUS, MATERIALS AND PROCEDURE.

THE apparatus employed in the operations to be described is, with very few exceptions, that available in any chemical laboratory. Glass vessels used for preparative work should, if possible, be of resistance glass; this applies even to test tubes used for such work as experiments on electrolyte coagulation. Test tubes which turn distilled water containing a little phenolphthalein pink in a very short time are by no means uncommon, and should not be used for any purpose. As regards the choice of larger vessels, it should be remembered that very thorough cleaning is necessary, and that in many cases undue exposure of solutions to air is undesirable, so that the choice will fall on tall cylindrical beakers, conical beakers with spout, or Erlenmeyer flasks. Flasks with narrow necks are, generally speaking, undesirable.

Vessels should be cleaned immediately after use, in any event, and again before use in the case of sensitive preparations. The methods to be adopted in the former case naturally depend to a great degree on the previous contents of the vessel. Suspensoid sols are, of course, easily washed off, although in

some cases—especially with positive sols—small quantities are adsorbed on the glass surface so tenaciously that washing with dilute hydrochloric or nitric acid may be required to remove the adsorbed film. Very thorough and repeated washing is necessary after emulsoid sols; it must be continued until the last water shows no trace of froth. Traces of gelatin, albumin, etc., allowed to dry in glass vessels are very troublesome to remove, and may require the use of nitric acid or hot dichromate-sulphuric acid mixture. Irreversible gels, *e.g.*, silicic acid, formaldehyde-gelatin, etc., should be made only in vessels from which the gel can be easily removed, such as cylindrical beakers, preferably with thick walls. Whatever the method of cleaning, the vessels should finally be rinsed thoroughly with distilled water and drained. Drying with cloths is to be avoided; drying with alcohol and ether is only necessary in the case of small apparatus used for quantitative work, *e.g.*, viscometers. Apparatus cleaned as described and kept with the opening downwards will generally require only rinsing with several lots of distilled water before use.

Operations like making up salt solutions of known concentration for the preparation of sols, electrolyte coagulation, etc., require the usual apparatus and call for no special remarks. Sols of emulsoids *containing a definite amount of dry material to a given volume of dispersion medium* also offer no difficulty. Substances which disperse in the cold, like albumin or gum arabic, stick to the walls of the vessel in the earlier stages of the process, but are easily detached when swelling has progressed sufficiently. The use of thick-walled vessels is, however, advisable, as thin beakers are easily broken in trying to detach fragments which stick obstinately. If sols containing a definite weight of substance *in a given volume of sol* are required, the procedure is a little more

difficult. For gelatin it is fully described under that heading; with materials like albumin, gum, etc., it will be found advisable not to make the sol directly in the measuring flask, as stirring is impossible. The weighed quantity of dry material should be placed in a beaker and dispersed with, say, 50 or 60 per cent. of the total volume eventually required, and the sol so obtained poured into the measuring flask. The beaker is then carefully rinsed with small successive lots of dispersion medium, which are poured into the flask: the aggregate volume of these washings must fall short of the mark by a few cubic centimetres. The flask is finally filled to the mark with the dispersion medium from a pipette and the contents well mixed. This method is not quite accurate, but the error is generally not as great as that due to the variable moisture content of the starting material.

Filtration will be necessary chiefly in the case of organic emulsoid sols. It is generally a somewhat tedious process and, whenever possible, should be left overnight. The residues which have to be removed are generally not crystalline, and the use of vacuum does not accelerate the rate of filtration materially beyond the first few cubic centimetres. Carefully folded filters may be used where only the filtrate is required, as the complete removal of residue from such filters is not easy. Ribbed or corrugated glass funnels utilize the paper surface better than smooth ones, but are not so easily cleaned. All funnels should have the spouts cut off quite short, say not more than 2 cm. below the cone, as the usual long spouts are difficult to clean. Fairly hard filter papers are advisable in most cases.

Small quantities of troublesome sols may be filtered through shredded asbestos with good results. This can be used in the ball tubes listed in most catalogues of chemical glassware in the following manner. A disc of silver foil is cut which will pass

easily through the upper part of the tube (Fig. 1), and this is perforated with a strong needle, being supported on a cork plate for the purpose. The disc is then placed in the lower part of the ball and pure shredded asbestos packed into it up to its junction with the tube. The asbestos must be introduced in small quantities, moistened with the solution to be filtered, and rammed down lighfly with a stirring rod; the exact degree of pressure required can be found only by experience. The tube is then filled with the liquid to be filtered and the first few cubic centimetres of filtrate returned to it, if turbid. Concentrated sols like those of albumin or gum arabic, if filtered in this manner, will, of course, generally be still opalescent, but will be sufficiently clear in moderate thicknesses to allow the effect of coagulants to be seen distinctly, and will be free from particles which would interfere with, say, viscosity measurements.

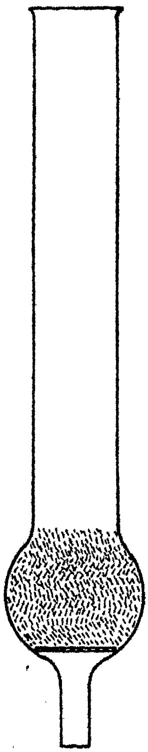


Fig. 1.

A centrifuge capable of dealing with at least 100 c.c. at a time will be found a very useful piece of apparatus, but is not indispensable.

A microscope provided with a $\frac{1}{4}''$ and a $\frac{1}{8}''$ objective and with at least one high-power eyepiece, is required for the examination of sols by dark ground and ultra-condensers. The special features of these appliances are fully dealt with in the section devoted to them, but a general knowledge of the microscope must be presumed.

As regards materials, the most important one is

pure distilled water. If a sufficient amount of conductivity water is available, all difficulties are avoided. It is, however, not essential for the work described in the following pages, and the extreme precautions taken in the case of a few preparations prominently mentioned in the literature have produced a somewhat exaggerated impression of the standard of purity required for less delicate work. Water distilled with ordinary care in reasonably designed apparatus will answer for all but a few purposes. Trouble is much more likely to be caused through the ordinary storage vessels, since they are very rarely made of resistance glass. If trouble is experienced, the first thing to do is to use *freshly distilled* water only, and to collect the small quantities which will be required in resistance glass flasks. Storage vessels coated inside with paraffin wax may be used; remember that the lining cannot be removed again by warming, as the glass cracks before the wax melts.

For the few preparations which require exceptionally pure water small quantities may be redistilled and condensed in a silver cooler. A thin-walled silver tube about $\frac{3}{8}''$ bore is not expensive, and can easily be fitted to a Liebig condenser in place of the glass cooler. There must, of course, be no parts on which water can condense, leading *down* the cooler: in other words, the cooler must be bent down to the distilling flask. This may be done by filling the tube completely with fine, dry sand, corking both ends and bending slowly over a cylindrical object of 3" or 4" radius. The water should be redistilled from, and collected in, resistance glass flasks.

It is hardly necessary to add that throughout this book water means distilled water of the standard quality available; where redistilled water is essential, or tap-water permissible, this is specially mentioned.

As regards the other materials, the ordinary chemicals call for no remarks. The solutions made from them for such investigations as electrolyte coagulation are *molar and not normal*, and this should be borne in mind. If there is any doubt about crystals containing the full amount of water of crystallization, or if the salts are anhydrous but hygroscopic, *e.g.*, $AlCl_3$ or $NH_4CNS$, the solutions must be standardized by the usual analytical methods.

Materials like gelatin, agar or dried albumin are not definite chemical individuals, differ slightly or even considerably when obtained from different sources, and contain an amount of moisture which varies perceptibly. The best that can be hoped for is concordant results; the first essential for this purpose is to use the same material throughout a given investigation and, therefore, to start with a sufficient stock to allow for all contingencies.

These considerations have an obvious bearing on the *degree of accuracy* to be aimed at in weighing and measuring. Centi- or milli-molar solutions of electrolytes may be made up with the same care as solutions for volumetric analysis, although the operations in which they are eventually used have not a sharp end-point. On the other hand, it is unnecessary (and will, fortunately, also be found impossible with many atmospheric conditions) to weigh 10 gm. of gelatin to fractions of a milligramme, since the moisture content may easily vary by 0·5 per cent. of the total weight in a very short time. No general rules can be given which would be an adequate substitute for the exercise of common sense in this respect.

A few general hints on procedure—many of which may appear superfluous to some reader or other, but have not been found so by the author—may conclude this introduction.

Read the whole chapter before beginning any of the work described in it; although the operations are generally put in the order in which they succeed one another, it is well to have a complete idea of the work before starting.

Many preparations change with age; do not make more than you require for immediate use or than will keep safely.

Label all preparations immediately in terms which, if not entirely correct technically, will remain intelligible to yourself. This is particularly important in the case of series, like solutions of different concentrations, Liesegang preparations, etc.

Adapt your methods to the peculiarities of your material. For instance, when told to dilute a 5 per cent. collodion with an equal volume of acetic acid, *do not put the highly viscous sol in the measuring vessel first and pour the thin solvent on it,* but proceed in the reverse order.

When an experiment fails, repeat it with the alteration of *one factor at a time*. If, *e.g.*, a gold sol turns out purple instead of red, try first a fresh beaker, than a fresh carbonate solution, and so on.

## CHAPTER II.

# DIALYSIS.

THE cheapest and most convenient membrane for dialysing any but small quantities—say 50 to 100 c.c. —is parchment paper. This is readily obtainable in sheets or cut in squares of various sizes. It varies a good deal in permeability, and only an actual trial can decide whether a particular sample is satisfactory for a given purpose. As the paper is fairly brittle in the dry state it should be kept flat or rolled, but never folded.

The classical method of employing the parchment membrane is that used by Thomas Graham, whose dialyser may be found in all catalogues of chemical apparatus. It consists simply of a glass cylinder open at both ends, one of which is provided with a rim or groove, over which the membrane is tied. A circular piece about 2″ larger in diameter than the cylinder should be cut and thoroughly soaked in water, placed centrally over the rim, carefully turned down over it all round, and then tied with a thin string. Unless this is done with care, leakage may take place through some of the folds formed; before a—possibly valuable—solution is placed in the apparatus it should, therefore, be tested by filling it with water and ascertaining that it does not escape. (*The same precaution applies to all dialysers to be described in this chapter!*) The dialyser is suspended or supported in a vessel filled with water, which is changed from time to time, or renewed continuously.

Parchment bags are preferable for larger quantities, as a larger surface is obtained in the same space. They may be made as follows: Cut a regular hexagon and soak it thoroughly in water. Then place it centrally on the bottom of an inverted beaker or jar, the diameter of which is about one-third of that of the *inscribed* circle of the hexagon. Gently pinch radial folds from the circumference of the beaker to the corners of the hexagon and mould them so that the paper midway between the corners touches the wall of the beaker, and then turn the folded portions over and smooth them into cylindrical shape. The whole procedure will be quite clear from Fig. 2, which shows the initial hexagon (dotted) and the final outline of the edge in plan, as well as a perspective view of the nearly completed bag on the beaker. The folds must not be sharp, as even wet parchment may be damaged by too drastic treatment. When the bag has been moulded as described, a string is *loosely* tied round it, or a *fairly slack* rubber band slipped over it within about 2″ of the edge, and the bag is then drawn off the beaker. Its permanent shape is secured by threading a clean, thin string through the folds, as indicated by dotted line in the plan, which is gently drawn tight after every completed stitch so that the circumference at the open end is approximately the same as at the bottom. The bag is suspended in a jar of suitable size by two or three strings tied at equal distances to the string which secures the circumference. The jar is then slowly filled with water, while the liquid to be dialysed is poured into the bag *at the same time and at about the same rate*, so as to keep the external and internal level nearly the same; in this way any strain on the mouth of the bag is avoided and it retains its shape. The water may be renewed from time to time, but it is preferable to use a continuous flow, as dialysis is greatly accelerated thereby. This

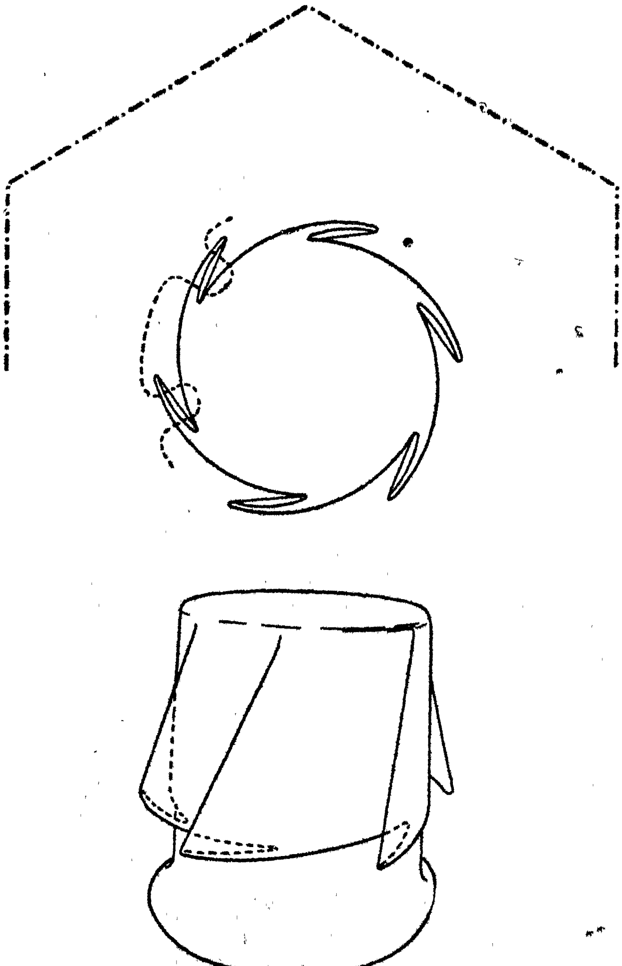
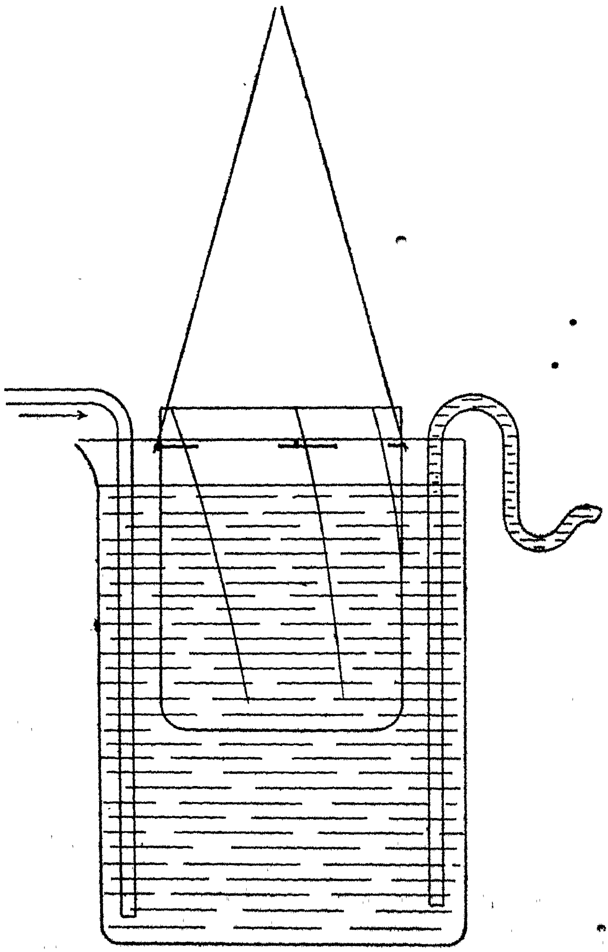


FIG. 2.

may be done by allowing water to flow into the outer vessel and removing it by means of a syphon, which must be of the type shown in Fig. 3, to avoid either the vessel or the syphon being emptied, if the water supply fails by any accident. The rate of supply must, of course, be so adjusted as not to exceed the rate of discharge from the syphon, since otherwise the water may flow over the top of the jar. It is hardly necessary to add that the same arrangement may be used with a Graham dialyser, and also, slightly modified, with many of the appliances yet to be described. Continuous flow can, of course, be used only when the liquid remaining in the dialyser is all that is wanted ; if it is, for any reason, necessary to examine the solution which has diffused through, dialysis must be performed with successive lots of water, which may be kept separate or be combined.

Parchment paper may also be obtained in the form of tubes—"sausage-skin dialysers" as they are usually termed in catalogues. They are sold flat, and in that condition are from 40 to 100 mm. wide, giving a diameter, when filled with liquid, of 25 to 70 mm. As they are easily damaged, any length selected for use should be carefully tested for leaks. It may be used in various ways : one of the simplest is to bend a (thoroughly soaked and tested) piece into U-shape and place it into a tall cylinder, allowing the open ends to project an inch or two. The tube is then slowly filled with the liquid to be dialysed, while the cylinder is at the same time filled with water at about the same rate, so that no strain is placed on the tube. Another method is to close one end of the tube by folding it over two or three times, the first fold being about 5 mm. wide, and securing this end with a rubber clip. The clip is made by cutting a rectangular strip about 20 mm. wide and about 25 mm. longer than the width of the (flat) tube



from white rubber sheet about 8 to 10 mm. thick, in which a central straight incision is made about 5 mm. longer than the width of the tube. This is then opened a little by inserting two thin pieces of stick at the ends, slipped over the folded end, and then closed by withdrawing the sticks. When the use of metal is unobjectionable one of the wire clips used for attaching papers to one another may be employed, or a similar clip bent from heavy silver or copper wire. The tube should be tested for leakage after being closed.

Finally, *seamless* thimbles of parchment papers can be obtained, which, although somewhat expensive, are reliable and extremely convenient, especially for the examination of small quantities of liquid. A simple method of using them is shown in Fig. 4. The thimble, filled with the solution to be dialysed, is placed in an Erlenmeyer flask of suitable size filled with the solvent. The parchment swells perceptibly in water, and the neck of the flask must, therefore, be a few millimetres larger in diameter than the (dry) thimble, to permit its easy withdrawal when it is saturated.

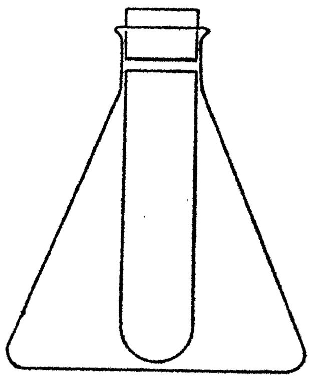


FIG. 4.

A number of natural membranes, such as goldbeater's skin, fish-bladder, etc., have been used for dialysis. Since they vary in permeability or require careful purification, their use can hardly be recommended except as makeshifts, especially in view of the comparative ease with which membranes of considerable uniformity and covering a great range of

permeability can be made by the methods to be now described.

These are based on the use of collodion, *i.e.*, sols of cellulose nitrate in a mixture of ether and alcohol. The raw material is obtainable commercially as "gun cotton" or "pyroxylin," and is generally sold damped with alcohol; it should be dried before weighing. The usual concentration is 3 to 4 gm. of gun cotton to 100 c.c. of ether-alcohol mixture, the proportions of the latter varying between 14 parts of alcohol (90 per cent.) to 86 of ether, and 25 parts of alcohol to 75 parts of ether; equal volumes of alcohol and ether have also been used, but this composition is unusual.

The weighed quantity of gun cotton is placed in a wide-necked bottle, the requisite volume of alcohol poured on it, the bottle corked and allowed to stand for about fifteen minutes. The ether is then added and the mixture stirred occasionally, until the gun cotton has dissolved; it should do so without leaving any residue. The sol should be almost clear and does not require filtering. One of the most convenient ways of employing it is to make dialysing thimbles by coating the *inside* of test tubes of suitable size; the beginner will find 20 mm. diameter × 125 mm. long a convenient size, although with practice much larger thimbles can be made without difficulty. The test tubes must be quite smooth on the inside, thoroughly clean and dry.

The selected test tube is filled with collodion, care being taken to pour it down the side so as not to form any air bubbles. The mouth of the test tube is then placed above that of the bottle and the collodion poured back slowly by slightly inclining the tube and rotating it constantly and slowly. The inclination of the tube is gradually increased as emptying proceeds, but not more than is necessary to allow the collodion to flow out in a thin uniform stream. If it

is raised too rapidly the bottom of the thimble is apt to be excessively thin. The tube is finally brought to a vertical position and the last remains of collodion, which should not then amount to more than a few drops, allowed to drip off, after which the layer left on the inside of the tube is allowed to dry for a short time. Although the degree of drying is the crucial point of the whole process, no definite rules can be given; the collodion should not stick to the finger when touched lightly, and should *just* be visible as a faintly bluish coating when the tube is viewed against a dark background. When this stage is reached the tube is submerged in water, care being taken to allow all air to escape, and is left for at least 15 minutes. The depth of water should be about 2" more than the diameter of the tube, so that the subsequent operation can be carried out without its being uncovered. After the minimum time of immersion has elapsed, the collodion film is detached round the edge of the tube, a finger inserted so as to touch the collodion skin, and the latter very slowly pulled out, while the test tube is held with the left hand. It must be remembered that the rate at which the collodion skin can be pulled out is fixed by the rate at which water can flow through the space between it and the wall of the test tube, which is necessarily slow; any attempt to hurry matters is fatal. If the bottom of the vessel containing the water is dark, the collodion membrane can be seen very distinctly, and the bottom end, which is the most likely portion to give trouble, watched.

The finished thimbles can be kept under water for several weeks, undergoing only slight changes in permeability. On the whole, however, it is advisable to make and use them fresh. They can be mounted in a variety of ways; a convenient method is to insert a short piece of glass tubing, the edge of which has been carefully rounded in the flame, and

to fix the thimble to it with collodion, or by tying; in the latter case a strip of gutta-percha tissue or oiled silk must be wound over the collodion to prevent it from being cut by the thread used for tying.

As has already been pointed out, the permeability of thimbles made from ether-alcohol collodion depends very largely on the extent of drying which they have undergone before immersion. The ether and alcohol still remaining in the film is replaced by water, and this fixes the permeability of the hydrogel of cellulose nitrate which ultimately constitutes the membrane. Although practice soon enables a careful worker to turn out fairly uniform thimbles, the whole difficulty can be avoided by the use of acetic acid collodion. This is made by dissolving 4 gm. of gun cotton in 100 c.c. of glacial acetic acid; lower concentrations give fragile films, while higher ones produce unnecessarily dense membranes. The test tubes are coated and the excess emptied in exactly the same way as described; the film is, however, not allowed to dry, but the coated tubes are *immediately* submerged in water. After about 30 minutes they may be withdrawn as explained, the operation being generally easier than with ether-alcohol collodion; they are then left in water, which is occasionally changed, until the whole of the acetic acid has diffused out, and may be preserved under water.

A very convenient way of making dialysing thimbles, which are less fragile and permit much greater variations in permeability than those just described, consists in impregnating the seamless thimbles of filter paper (Soxhlet thimbles) made in various sizes for fat extraction. One of these is held vertically over a small dish and filled to the top with collodion; when the liquid has penetrated over the *entire surface*, it is inverted and drained with constant turning. If acetic acid collodion is used, the

thimble is then submerged in water immediately; with ether-alcohol collodion it must, like the thimbles formed in test tubes, be allowed to dry for a few minutes before immersion. Since the mechanical strength is provided by the filter paper, collodions of low concentration may be employed, 2 per cent. in either acetic acid or ether-alcohol being sufficient for most purposes. The thimbles are strong enough to stand upright, and may be used like parchment paper thimbles. A convenient method of using any type of thimble is to stand or suspend it in a cylindrical vessel of slightly larger diameter, provided with an inlet at the bottom and an overflow outlet at a level 1 to 2 cm. below the top edge of the thimble. Water is continuously passed in at the bottom and overflows at the top, and dialysis proceeds with great rapidity with comparatively small quantities of water.

Flat membranes of (ether-alcohol) collodion are rather easier to make than thimbles, and can conveniently be used for continuous dialysis in the "Star Dialyser" described by Zsigmondy. The apparatus (Fig. 5) consists of two parts, both of ebonite, a disc provided with a rim about 10 to 15 mm. deep, and a cylinder which fits loosely into the latter, open at both ends and 30 to 40 mm. deep. The disc has a central inlet and its upper face is provided with six or eight ribs, about 3 mm. deep, which stop a few millimetres short of both the central opening and of the rim. To prepare the membrane the ring is placed on a clean piece of plate glass and sufficient collodion poured into it to cover the glass to a depth of 2 or 3 mm. The ring is lifted slightly, to allow the collodion to penetrate between it and the glass; to strengthen the joint thus made, the outside of the ring is painted with collodion to a height of about 5 mm. from its lower edge. After the collodion has dried some minutes water is poured into the ring, which, together with the collodion mem-

brane adhering to it, can be lifted off the glass after about 10 or 15 minutes. The ring is then

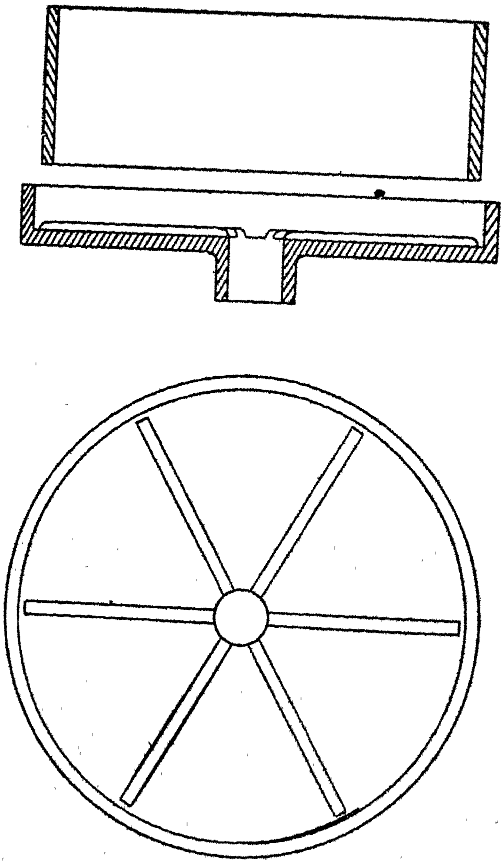


Fig. 5.

placed into the disc, filled with liquid to be dialysed, and water is passed through the central inlet, which

overflows round the edge of the rim. As it is difficult to adjust the apparatus so exactly that overflow is uniform all round the rim, it is best to localize it by means of two or three strips of filter paper, placed between the open cylinder and the rim and bent over the latter, so as to act as syphons.

Special arrangements are necessary when the sol to be dialysed has an appreciable osmotic pressure, as is the case, *e.g.*, with albumin sols. In this case water flows into the dialyser, diluting the sol and eventually causing it to overflow. The only way to prevent this is to counterbalance the osmotic pressure hydrostatically; in other words, to keep the level of the sol in the dialyser above the water level outside from the beginning. For small quantities, such as come into question here, the simplest arrangement is that shown in Fig. 6. A dialysing thimble of either parchment or paper impregnated with collodion is fitted with a rubber stopper and tied tightly; a strip of gutta-percha tissue about 15 mm. wide is first wound round the end of the thimble and strong thread tied over this. Through the rubber stopper passes a funnel tube about 30 cm. long, which must have a diameter of at least 8 mm., so that the sol can be poured down one side of it, allowing the air to escape and the thimble and tube to be filled to the top. The thimble is submerged in a beaker through which water flows continuously. With this arrangement

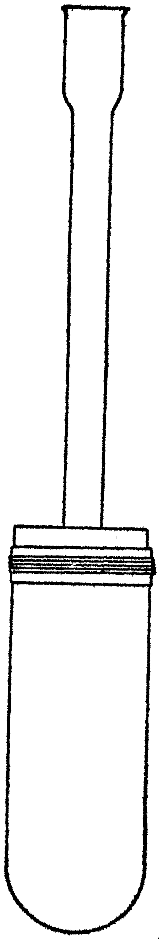


FIG. 6.

the liquid remains at its original concentration and the bulk of it is still contained in the dialysing membrane, as the volume of the funnel tube is comparatively small.

## LITERATURE.

Membranes made from collodion of unusually high concentration and capable of standing considerable pressures are described by A. T. Glenny and G. S. Walpole, *Biochem. Journ.*, IX., 284 (1915); G. Wegelin, *Koll.-Zeitschr.*, XVIII., 225 (1916), a new method of rapid dialysis and ultra-filtration.

## CHAPTER III.

## SUSPENSOID SOLS.

### A. METALLIC SOLS.

*Gold Sols.*—A 1 per cent. solution of gold chloride (more correctly, auro-chlorhydric acid, $HAuCl_4 . 3H_2O$) serves as the starting material. The "gold chloride" of photography, $NaAuCl_4 . 2H_2O$, may be used instead for all the methods, with the exception of Zsigmondy's; a 1 per cent. solution of this salt is obtainable in commerce. For the method first described, reduction by tannin, the gold chloride must be made exactly neutral to litmus by addition of sodium or potassium carbonate (N/5 solution).

*Reduction by tannin* (Wo. Ostwald). Dissolve 0·1 gm. of purest tannin in 100 c.c. of water. If this solution is to be kept it should receive an addition of a few drops of chloroform, without which it goes mouldy.

Dilute 1 c.c. of the gold chloride solution with 200 c.c. of water, stir and add 1 c.c. of the tannin solution, then warm over a Bunsen burner. Reduction gradually proceeds and the liquid becomes red. Continue heating and, when the liquid boils, add another cubic centimetre of gold chloride solution, followed by a cubic centimetre of tannin. The resulting sol should be perfectly clear in transmitted light and of deep ruby-red colour. The mixture must be well stirred after every addition.

Sometimes the colour of the liquid containing the first lot of gold chloride and tannin does not become red while warming, but purple, or even a cold violet.

Do not be deterred, but continue to heat to boiling; after the second addition of gold chloride and tannin at boiling point the colour very generally changes to red without even a tinge of purple.

Reduction may also be carried out in the cold by using a larger proportion of tannin solution, say 100 c.c. of water, 1 c.c. of gold chloride solution, and 3 to 5 c.c. of tannin solution, added gradually. In this case the sol is more liable to have a purple or bluish tinge.

Sols made by these methods are liable to the growth of mould on keeping and gradually lose colour, the gold being deposited on the mycelium of the mould. This trouble may be prevented by adding a few drops of chloroform, or, in view of the great simplicity of the method, by preparing the sols when and as required. These sols are protected to a slight and uncertain extent by the tannin and its oxidation products, and are less suitable for coagulation experiments than the following.

*Reduction by formaldehyde* (R. Zsigmondy). Heat 120 to 150 c.c. of redistilled water in a 300-c.c. beaker; while it is warming add 1 c.c. of gold chloride solution (1 per cent.), and then 2·5 to 3 c.c. of a N/5 solution of purest potassium carbonate. As soon as the solution boils stir vigorously; add gradually, but fairly quickly, 2 to 3 c.c. of dilute formaldehyde solution (1 c.c. of commercial 40 per cent. formalin to 100 c.c. of water) and extinguish the flame. Reduction is complete in about a minute, and the resulting sol should be perfectly clear in transmitted light and of pure ruby-red colour without purple tinge.

The beaker used should be of resistance glass, and stirring rods of the ordinary soft glass must not be used; a tube of resistance glass closed at one end should be used for stirring. The sol should also be kept in vessels of resistance glass.

For some reason, which is still obscure, *larger batches than about 150 c.c. cannot be made successfully.* If larger quantities are required, they must be made in 150 c.c. lots as described ; since all the solutions can be made up in large quantities and keep indefinitely, there is no difficulty in preparing any volume of sol likely to be required.

The sol can be dialysed against redistilled water, but will keep without this being done in vessels of resistance glass. It is very suitable as a standard preparation for experiments on electrolyte coagulation, protection, etc.

*Palladium Sol.*—This can be prepared by exactly the same procedure as Zsigmondy's gold sol, using the following quantities : 150 c.c. of water, 1 c.c. of 1 per cent. palladium chloride solution, and 0·4 c.c. of N/10 sodium carbonate solution, reduced by 3 to 4 c.c. of dilute formaldehyde (1 c.c. of commercial formalin to 100 c.c. of water). The sol should be brown and perfectly clear in transmitted light.

*Silver Sol.—Reduction by dextrine* (Carey Lea's method). This is one of the best examples of a highly concentrated metallic sol, as concentrations up to 5 per cent. of Ag can be obtained in favourable conditions. The following quantities should be tried first, but there is no difficulty in dealing with four or five times these amounts.

Dissolve 4 gm. of commercial dextrine in 100 c.c. of water and then 4 gm. of purest caustic soda. Dissolve 3 gm. of silver nitrate in 20 c.c. of water and add to the dextrine-soda solution. A precipitate of silver oxide forms, which is gradually reduced by the dextrine, the colour changing to a reddish-brown. Allow 20 to 30 minutes for this, and then add 100 c.c. of 96 per cent. alcohol and stir. Allow the mixture to settle for another 15 to 20 minutes, and then pour off the turbid liquid from the sediment of silver as completely as possible. On pouring on

water the silver generally disperses immediately; should this not be the case, a little shaking and stirring will be sufficient to induce dispersion.

The silver amounts to 1·81 gm., and in favourable conditions 35 to 40 c.c. of water will disperse the whole of it, so that the sol contains about 5 per cent. of disperse phase. It is, however, advisable to use a greater volume of water, say about 180 c.c. This sol is dark brown and opaque even in thin layers; when diluted with about 50 times the amount of water it should be clear in transmitted light, with a greenish-black surface colour in reflected light. The colour of the sol, and in fact the success of the whole method, depends a good deal on the quality of the dextrine, which can be determined only by experiment. Generally speaking, the ordinary yellow commercial brands work better than a highly purified product. The 1 per cent. sol may be kept unaltered for a long time.

*Reduction by tannin.* Add to 100 c.c. of water 1 c.c. of 1 per cent. silver nitrate solution, and then a few drops of weak ammonia. Reduce with 3 to 4 c.c. of 0·5 per cent. tannin solution. The sol should be brown and perfectly clear in transmitted light, with a marked green surface colour in reflected light.

*Reduction by hydrogen* (Kohlschuetter's method). This process is of interest as giving an electrolyte-free sol. Dissolve 1 gm. of silver nitrate in 20 c.c. of water and precipitate with a slight excess of caustic soda. Wash the precipitate of silver oxide by repeated decantation with hot water, and then suspend it in 200 c.c. of redistilled water, shake well, and then filter off any undissolved oxide. Pour the solution into a resistance glass flask kept at 56° to 60° C. in a water bath (or thermostat), and pass a current of hydrogen through it by means of a tube of resistance glass. Reduction is complete in 20 to 25 minutes.

*Other methods.* As gold chloride is reduced by most reducing agents, a very large number of methods of preparation of gold sols are possible; references to some of these are given at the end of this chapter. Generally speaking, sols will result if gold chloride solutions containing about one part in 10,000 are treated with small quantities of the following reducing agents, in solutions containing from one part in 4,000 to one in 500: gallic acid, hydroquinone, pyrocatechin, white phosphorus in ether (Faraday's method, developed by Zsigmondy, *q.v.*), hydrazine hydrate (Gutbier), phenylhydrazine hydrochloride (Gutbier and Resenscheck), etc. Silver may similarly be reduced from dilute silver nitrate by ferrous citrate (Carey Lea), in alkaline solution by hydrazine hydrate, all photographic developers, etc.

## B. Sulphide Sols.

*Cadmium Sulphide Sol.*—This is an instance of a sol produced by peptisation of a coarse precipitate.

Dissolve 0·5 gm. of cadmium chloride in 20 c.c. of water and precipitate with moderately concentrated ammonium sulphide. The precipitate should be a deep yellow and should settle rapidly; if it does not, the ammonium sulphide solution requires diluting. Wash the precipitate by decantation with two or three lots of water, 50 c.c. each, and suspend in 300 to 400 c.c. of water. Pass a slow stream of hydrogen sulphide through the mixture and shake occasionally. The suspension first becomes milky, then yellow and moderately clear, and after 20 to 25 minutes most of the precipitate will have been dispersed. The sol may be filtered to remove any remains of precipitate, and boiled to drive off the excess of hydrogen sulphide, without coagulation occurring. The filtered sol is a pale golden yellow

in transmitted light, with marked greenish opalescence in reflected light.

*Arsenic Sulphide Sol.*—This sol has been the subject of many classical investigations, especially on electrolyte coagulation. To prepare it, dissolve 2 gm. of arsenic trioxide in one litre of water; keep the latter boiling until solution is complete. After cooling the liquid pass a slow stream of hydrogen sulphide through it, with occasional stirring, until the colour does not deepen perceptibly. The sol is a pale orange colour in transmitted light, with a greenish-yellow opalescence in reflected light. Excess of $H_2S$ can be removed by passing hydrogen through the sol; this must be done if the sol is to be used for coagulation experiments.

## C. Miscellaneous Preparations.

*Prussian Blue Sol.*—Dissolve 0·4 gm. of crystallized potassium ferrocyanide in 20 c.c. of water and 0·4 gm. of ferric chloride in 20 c.c. of water. Pour *the first solution into the second, slowly and without stirring.* Allow the mixture to stand for a few minutes and then pour it on a folded filter of hard paper. The filtrate should be quite clear and run fairly freely. When filtration is complete, wash the precipitate with four successive lots of 25 c.c. of water.

The precipitate is then dissolved in 300 c.c. of solution containing 16 gm. of crystallized oxalic acid. The simplest way to do this is to pour the acid solution on the filter and allow it to percolate; the precipitate will be found to have been completely dissolved when the whole volume of acid has passed through the filter. The solution of Prussian blue in oxalic acid is then dialysed in a parchment bag against repeated changes of distilled water, until the

last batch of the latter gives no perceptible oxalate reaction. Owing to its deep colour and sensitiveness the sol is very suitable for cataphoresis and coagulation experiments. For the latter purpose the sol can be diluted with an equal volume of water, as even in that dilution it is deeply coloured in a thickness of 1 cm. The concentrated sol is quite stable, and there is, therefore, no reason for making a dilute sol directly, as this course entails waste of oxalic acid.

*Ferric Hydroxide Sol.**—Heat 500 c.c. of water in a tall beaker and, when it is boiling vigorously, add 2 c.c. of a 30 per cent. solution of ferric chloride, gradually and with stirring. The liquid turns a deep reddish-brown and remains perfectly clear.

The sol contains HCl, corresponding to 0·6 gm. of $FeCl_3$, *i.e.*, about 0·4 gm., or approximately 22 millimoles per litre. As this is a small fraction only of the HCl concentration required for coagulation, the sol may be used for precipitation experiments without being dialysed, as well as for cataphoresis in the U-tube (no particles are visible with dark-ground illumination, so that the microscopic method is not applicable). Most of the HCl can be removed by dialysis in the parchment bag, but only experience will tell how far dialysis may be continued without coagulation of the sol. Both the acid and the dialysed sol keep indefinitely. Only the latter is suitable for experiments on the mutual coagulation of oppositely charged sols.

## LITERATURE.

For all inorganic suspensoid sols: Th. Svedberg, "Die Methoden zur Herstellung kolloider Loesungen anorgani-

* Although this sol has some emulsoid properties, it is classed here with the suspensoids on account of its behaviour to electrolytes, etc.

scher Stoffe," Theodor Steinkopff, Dresden, 1909. Sols with unusual electric charges: H. S. Long, *Proc. Univ. of Durham Phil. Soc.*, V., Part 2 (1913), positive red gold sol; F. Powis, *Journ. Chem. Soc.*, 107, 818 (1915), negative ferric hydroxide sol. Dye sol with characteristic suspensoid properties: Wo. Ostwald, *Kolloidchemische Studien am Kongorubin*, *Koll. Beihefte*, X., 179 (1919).

CHAPTER IV.

## SUSPENSIONS.

*Mastic Suspension.*—This preparation is one of the classical subjects of investigation. Dissolve 0·1 gm. of powdered gum mastic in 10 c.c. of alcohol or acetone. Pour the solution slowly into 500 c.c. of water, stirring the latter vigorously. Filter the suspension through a fairly close filter paper to remove coarser particles.

The preparation is almost opaque, with vivid pale blue opalescence, in reflected light, and should be perfectly clear and a faint yellow in transmitted light. It shows an extremely bright blue Tyndall cone.

Coagulation experiments should be made with HCl and with salts of uni-, bi- and tri-valent cations, as the suspension behaves somewhat differently from suspensoid sols (see chapter on Electrolyte Coagulation). "Titration" will be found somewhat difficult, as there is no marked sudden change; on standing, however, the disperse phase separates very clearly as a flocculent precipitate, though sedimentation is naturally slow. In the U-tube a sharp boundary will be seen if observed in *reflected* light.

A similar suspension, using exactly the same quantities, may be made from other resins. The beginner will find dragon's blood convenient, as the colour is a vivid red.

Gamboge may be treated in the same way. A suspension which shows the Brownian movement, cataphoresis under the microscope, etc., can also be

made by rubbing down a stick of the gum with a few cubic centimetres of water in a saucer (as is done with sticks of Chinese ink), diluting the resulting mixture with a large volume of water and filtering to remove coarser particles.

CHAPTER V.

# ORGANOSOLS.

THE most convenient method of directly preparing organosols of the noble metals is that of C. Amberger, in which wool-fat (lanoline) is used as protective agent.

To prepare silver sol, dissolve 3·5 gm. of silver nitrate in 5 c.c. of water and add this solution in very small quantities at a time to 15 gm. of cold lanoline, incorporating it thoroughly with the latter by means of a pestle or a silver spatula. The success of the subsequent reduction depends on the completeness with which this is done. If any silver nitrate is left in the form of drops, the oxide and silver formed from them are of course not protected by the wool-fat and remain as a coarse insoluble residue when the latter is taken up in an organic solvent. Then add in the same way a solution of 1 gm. of sodium hydroxide in 5 c.c. of water. The mass turns first yellow and then brown, owing to the formation of silver oxide. On standing in the light the latter is reduced to silver; the reduction is accelerated by gentle warming and by turning over the mixture from time to time, so as to expose the whole of it to the light. After about six hours reduction is generally complete, and the product is dissolved in 50 c.c. of chloroform. Fifty c.c. of petroleum ether and about 25 gm. of fresh granulated calcium chloride are then added—the latter to remove water, etc.—and the mixture allowed to stand for five to six hours. The solution, which should be a clear reddish-brown

when diluted with about 20 volumes of solvent, is then poured off; the solvent may be allowed to evaporate, leaving a mass of colloidal silver in wool-fat of the original salve-like consistency. This dissolves easily in ether, petroleum ether, also in fatty oils and in paraffin.

Organosols of gold, platinum and metals of the platinum group may be prepared in similar fashion, for which the original papers should be consulted.

LITERATURE.

C. Amberger, *Koll.-Zeitschr.*, XI., 97, 100 (1912), silver and gold; XIII., 310, 313 (1913); XVII., 47 (1915), platinum and metals of the platinum group.

## CHAPTER VI.

# EMULSOID SOLS AND GELS.

### A. SILICIC ACID SOL AND GEL.

A CONVENIENT starting material is a solution of sodium silicate having a density 1·16, made by diluting the commercial water-glass syrup with *freshly boiled* distilled water. The ratio of syrup to water is best ascertained by preparing a small lot, sufficient for determining the density with a spindle. The solution may be prepared in large quantities, and should be kept in a bottle closed by a rubber stopper or a glass stopper well rubbed with vaseline.

To prepare a sol, dilute 30 c.c. of concentrated hydrochloric acid (1·2 sp. gr.) with 100 c.c. of water, and pour 75 c.c. of the sodium silicate solution *into the dilute acid.* The mixture is dialysed in a parchment bag against repeated changes or against running water; the beginner will find the former course more satisfactory. Experience will show how far it is possible to push dialysis without the sol setting to gel prematurely in the dialyser.

The sol should be perfectly clear and colourless. It will keep for a length of time which can be ascertained only by experience; as the removal of gel, formed accidentally, from flasks or bottles with narrow necks is inconvenient, sol under examination should be kept in wide-mouthed bottles or taper beakers.

Setting is greatly accelerated by $CO_2$, carbonates, phosphates, and free alkali. The effect can be demonstrated by bubbling $CO_2$ gas through the sol

until the bluish tinge, which indicates the beginning of gelation, appears; or by adding small amounts of *dilute* solutions of carbonate, phosphate or ammonia to the sol, gradually and with constant stirring, which is discontinued as soon as the sol appears bluish. If the solutions are too concentrated, or are added too rapidly, local coagulation and flocculation may occur instead of complete gelation.

The concentrations given above are fairly high and will be found useful if a stiff gel is required. If the sol alone is wanted and requires keeping for some time, the same quantities of hydrochloric acid and of silicate solution should be used, but a larger volume of water.

To determine the amount of $SiO_2$ in a given sol, evaporate 5 c.c. *slowly* in a weighed crucible to dryness and then ignite until the weight is constant. In the later stages of drying gelation may occur, and the steam bubbles formed in the gel burst violently and may scatter some of the material, unless drying proceeds very slowly.

The effect of lyotropic additions is the same as in the case of other emulsoid sols. This can be shown qualitatively by placing 10 c.c. of freshly dialysed sol in each of three test tubes, keeping one as blank and saturating the others respectively with sodium sulphate and with ammonium thiocyanate. The sol containing $Na_2SO_4$ will set before, and that containing $NH_4CNS$ after, the blank sample; the latter very generally does not set at all.

*All vessels, measures, etc., used for sodium silicate or silicic acid sol should be washed immediately and thoroughly.*

## B. Gelatin and Agar Sols and Gels.

Gelatin occurs in commerce as "leaf" gelatin in sheets about 9″ to 10″ long by 4″ to 5″ wide, showing

the diamond-shaped marks of the wire netting on which the leaf has been dried; as powder, and as foil of uniform thickness—about 0·15 mm.—without any marks. The most suitable brands for practically all the work to be described are Coignet's "Photographic" and "First Quality," and Nelson's "Crystal Leaf." Since different brands differ appreciably in their physical constants and in their ash content, it is essential to start any given investigation with an amply sufficient stock of the brand selected. If great constancy is aimed at, it is desirable to take leaves at random throughout a one-pound package, or to shear through the entire package and use the strips so obtained rather than the necessary number of adjacent leaves.

For many purposes, *i.e.*, in all cases in which only *reproducible* and not *quantitative* results are aimed at, sols and gels containing a definite amount *to* a given volume of water, *e.g.*, 10 gm. of gelatin to 100 c.c. of water, are quite suitable and are easier to prepare than sols containing a specified amount *in* a definite volume of sol. The leaf is broken into pieces preferably not larger than $\frac{3}{4}''$ square, placed in a beaker, and the requisite amount of water poured on, care being taken that the whole of the leaf is covered; air bubbles should be removed by shaking or stirring. The gelatin is then allowed to swell, either to complete saturation, or for any arbitrarily fixed period, which, however, should not be less than two or three hours. Complete swelling may take 24 hours or even more; as gelatin imbibes something like ten times its weight of water, there will be no loose or unimbibed water, if the amount originally put on was less than ten times the weight of gelatin leaf. The thickened edges of the leaf take considerably longer to swell than the rest, and care should be taken that the time allowed is sufficient to soften them completely.

The next operation is the dispersing of the gelatin, which should be carried out on the water bath. A temperature of 35° to 45° C. is sufficient, but higher temperatures may be used to accelerate the process and for other reasons. Thus, if the sol is to be filtered (see below), it will be advisable to heat up to 80° or 90°, as otherwise the viscosity is high and the rate of filtration excessively low. *It is necessary to bear in mind that the properties of a gelatin gel or sol are not merely functions of the concentration and temperature, but depend on its whole previous history, viz., the period allowed for swelling, the temperature at which the sol was formed and the length of time during which it was exposed to this temperature.* To eliminate differences in the history, the practice is sometimes adopted of heating the sols for a definite time, say five minutes, to 100°, cooling at a definite rate to the temperature at which the sol is to be used (*e.g.*, for viscosity measurements) and keeping the sol at the lower temperature, likewise for a definite time, before use. While this treatment goes a considerable way towards obliterating the "thermal history," it is yet safer to adopt a rigidly uniform procedure in any particular investigation.

The sol in many cases does not require filtration and is ready for use when the gelatin is completely dispersed. If the gel is wanted especially for the study of its elastic or optical properties, it must not be used for at least four hours after setting is apparently complete, as the modulus and the accidental birefringence do not attain their final values before that time. Bodies of gel of definite shape can be made by pouring the sol into suitable moulds; thus cylinders can be made by using glass or metal tubes closed at one end, from which the gel cylinder is moved by dipping them into boiling water and lowing the gel to drop into an ample depth of cold ıter. Other shapes, *e.g.*, prismatic ones, can be

cast in moulds made from heavy tin or lead foil, or wooden moulds lined with ordinary tin foil, which is rubbed with vaseline, any excess being removed by wiping with cotton-wool. In all cases the gel should be left in the mould for several hours after setting, as mentioned above.

In many cases, and always when a salt capable of forming a precipitate with calcium salts, chlorides, sulphites or sulphates has to be added, the sol will require filtering. The most suitable paper is Chardin's, either the original brand or an imitation made in England. It can be obtained in sheets or as folded filters, which, however, are too large for the small batches usually required. Folded filters should be made, great care being taken with the point; as the paper is rather thick it is not advisable to try to make more than twelve folds. A hot-water funnel is used; those usually obtainable have the defect that the spout of the glass funnel is much too long, so that cooling and even setting may take place in the portion which passes through the stopper of the water-jacket. To obviate this, a rather thin stopper, not more than $\frac{3}{4}''$, should be used, and the spout of the glass funnel cut off so as just to project through the stopper. The temperature of the water bath should not be higher than is necessary to secure a reasonable rate of filtration; this varies considerably with different brands of gelatin and, when solutes are present, with the nature of the latter.

Gelatins are classified as "hard" and "soft," the former type being desirable for most investigations. The term "hardness" denotes a complex of qualities, among which are high "melting" and "setting" temperature and high elastic modulus. The melting and setting points are, of course, not strictly defined, and can be determined and compared only by conventional methods. An apparatus suitable for this purpose is illustrated in Fig. 7. A test tube A is

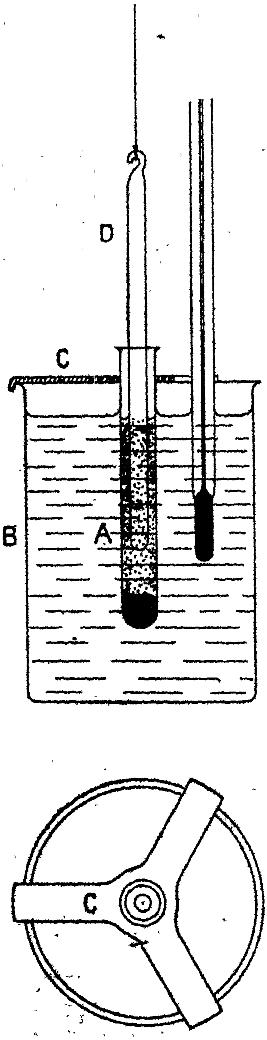



FIG. 7.

suspended in the centre of a 300 or 400 c.c. beaker B, which serves as a water bath, by means of the guide C, through which it must slide freely. A tube $\frac{5}{8}''$ diameter $\times$ 6″ long is suitable; it is weighted with 15 to 20 gm. of mercury. It is essential that the tube should be perpendicular when it is resting on C; if the rim is not sufficiently regular to ensure this, a square collar, say of rubber, should be used and permanently attached to the tube. A glass rod D, about $\frac{3}{8}''$ diameter for a $\frac{5}{8}''$ tube, is suspended exactly in the axis of the test tube. (If the apparatus is to be used frequently, it is advisable to mount it permanently to ensure correct alignment.)

To determine the melting point the test tube is filled with a definite quantity of the gelatin sol under examination, the beaker filled with water at a definite temperature, say 15° C., and the sol allowed to set for a definite time. The rod, with the test tube hanging to it, is now raised a definite height (which stage is shown in the illustration), and the temperature of the bath slowly raised, with constant stirring, until

the test tube slides off the gel cylinder surrounding the rod and comes to rest on C. The temperature at this moment is noted as the "melting point." If the "setting point" is also to be determined, the rod is lowered to its original position, the flame extinguished, and the bath allowed to cool. The rod is raised very slightly from time to time, until it just lifts the test tube with it, the temperature at this point being noted as the "setting point." It must be remembered that there is considerable hysteresis and that the setting point of harder brands may be as much as 7° or 8° C. lower than the melting point of about 10 per cent. gels.

A more delicate method of determining, with very simple means, the setting point is based on the well-known fact that the exposed surface of a gelatin gel which has been allowed to set quietly is *not smooth like that of a liquid, but shows a network of wrinkles.* The formation of these wrinkles is not due to drying, but occurs actually during the last stage of setting. The alteration in the appearance of the surface is very striking if it is observed under an acute angle in reflected light, and it may be used for determining the setting point in the following manner: A small porcelain crucible is filled with about 10 c.c. of sol and the bulb of the thermometer completely immersed in the latter. The reflection of the window in the surface is then observed, attention being fixed on some dark object in the light field, such as the window-frame or the like. The reflection of such an object is, of course, distorted by the menisci formed by the sol at the wall of the crucible and the stem of the thermometer, but is a smooth and unbroken curve. As soon as wrinkling commences, the image is broken up into fringes (see Fig. 8, *a* and *b*); the fall of temperature between the time when this alteration in appearance becomes barely perceptible and when it is quite unmistakable rarely amounts to

more than 0·1°, which is a more than sufficient accuracy.

As regards other physical properties of the sol, the one most likely to require investigation is its viscosity at different concentrations and temperatures. The methods to be employed are described fully in the chapter dealing with viscosity measurements. Since viscosity is particularly sensitive to variations

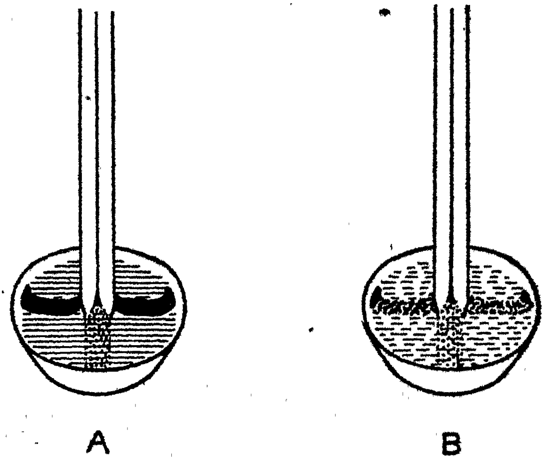



FIG. 8.

in the "thermal history," uniformity of procedure in the preparation of sols for this purpose must once more be insisted on as being of fundamental importance.

As regards the gels, reactions in gels are treated in a separate chapter. The quantitative study of the modulus of elasticity or the accidental birefringence produced by strain is beyond the limits of this book. It is, however, easy to demonstrate the latter by very simple apparatus, if a Nicoll and selenite plate are

available, and the study, particularly of the strains set up by drying, is instructive. The apparatus is simply an open box (Fig. 9) about 16″ high × 8″ wide. Two glass plates—photographic plates from which the film has been removed are suitable — rest on the bottom, inclined under an angle of about 53° with the latter. A strip of either ground-glass or glass coated on the lower side with the "matt varnish" used in photography rests on two ledges, about 9″ or 10″ from the top of the box. An opening in the centre of the top takes the mount of the Nicoll prism, which can be rotated. If light from a lamp placed as shown is reflected from the double glass plate, sufficient fraction of it is polarized to show very slight strains in gelatin gels containing 10 per cent. and more.

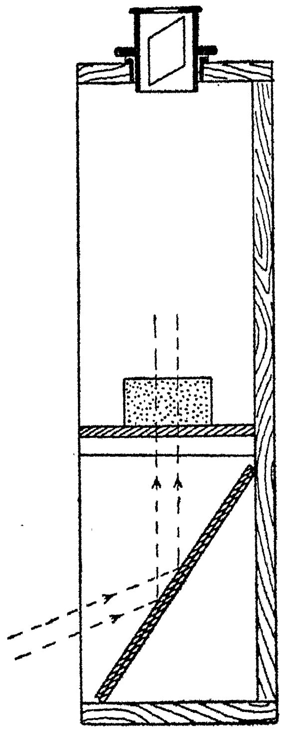


FIG. 9.

The strains set up during drying and their progressive changes can easily be traced and are instructive. A body of gelatin gel, unless it is a simple surface of revolution approximating fairly closely to a sphere, does not remain similar to itself during drying, and if the surfaces meet in edges very considerable distortion occurs. Thus, a right cylinder with flat ends has two circular edges, and drying is at first much more rapid along these than it is on the

curved or flat surfaces. The edges, therefore, contract and the cylinder becomes a barrel with convex ends. The edges have now become so dry and rigid that very little further drying takes place in them, while the rest of the surface is rapidly shrinking, and the final shape is a single-shell hyperboloid with concave ends. Similarly, when a cube is allowed to dry, the edges contract first and the faces become convex, while the final surface has concave faces with, of course, concave edges. The distribution of strain, and the change from compression to tension, can easily be observed and analyzed.

Gelatin being highly liable to putrefactive changes, neither sols nor gels can be kept for long without sterile precautions, which are beyond the scope of this work. Hardening agents like formaldehyde alter the physical properties of gelatin so much that they are suitable only for preserving finished specimens. Directions will be found in the chapter on the Liesegang phenomenon.

*Agar* occurs in commerce as strips having a fibrous texture, as a fine powder, and as bars of square cross-section. The first-named is the cheapest form; powdered agar has the advantage that the time necessary for swelling is considerably reduced. If strip is used it is torn into small pieces, which are allowed to swell in the requisite volume of water for about 24 hours. A small addition—one part in 500—of acetic acid is usual and promotes imbibition, but is not essential. The mixture is then boiled slowly, until the shreds have entirely disappeared. The sols are always turbid and show even macroscopic fibres and fragments, so that they must at least be strained through fine muslin or through glass or cotton-wool plugs. If clearer sols and gels are required they must be filtered through Chardin paper in the manner described for gelatin; the water in the jacket must be boiling. With sols containing

1 per cent. and over filtration is tediously slow, and the filtrate sets long before the filtration of even small batches is complete. If a large drying oven or sterilizer kept at 100° C. is available, the most convenient course is to place the whole apparatus, *i.e.*, filter funnel and beaker or flask for the filtrate, into it, when the whole can be left to itself without further attention. The setting temperature of agar sols is between 35° and 40°, while the melting point of gels lies between 90° and 100°, so that gels have to be heated on a water bath at boiling point to obtain a sol. Agar gels are not liable to putrefaction and are, therefore, preferable to gelatin for long-continued experiments—*e.g.*, on diffusion—in which the specific properties of the gel are of no consequence. They are, however, a good medium for the growth of various moulds and occasionally of *Bacillus prodigiosus*, which latter forms red patches. Both occur chiefly on the surface, and the rest of the gel may generally be used after the affected patches have been cut away.

Agar gel, unlike gelatin, does not adhere to glass, and specimens may be removed from moulds without the heating necessary in the case of the latter. Thus cylinders may be cast in tubes stoppered at the bottom, and will drop out when the stopper is removed. A certain amount of liquid, which also contains agar, exudes from agar gels on standing, partly on the surface and partly between the gel and the containing vessel. This is a normal phenomenon and does not indicate faulty procedure in the preparation.

*The Lyotropic Series.*—It is desirable to demonstrate the general nature of the series by showing its effect on two sols as chemically different as gelatin and agar. Sulphates, chlorides and thiocyanates may be chosen as representative specimens, sufficient of each being placed into a 100-c.c. beaker to

produce a concentration of N/2 in 50 c.c. of sol (allow for water of crystallization!). Each of the beakers so prepared now receives 50 c.c. of sol, 10 per cent. gelatin sol and 1 per cent. agar sol being suitable, and the same quantity of pure sol is placed into a fourth beaker for comparison. All four beakers are placed in the water bath until they have attained the same temperature and are then taken out and allowed to cool. The water bath should be at 35° to 40° C. for the gelatin sol and at boiling point for the agar sol. The order in which the gels set will be the same for gelatin and agar, and the intervals between the four specimens will be considerable; the sol containing thiocyanate remains liquid at room temperature.

The effect of the lyotropic series, and also that of dilute acid and alkali, on the swelling of gelatin may also be demonstrated very simply in the following manner. Squares having a side of, say, 15 mm. are cut from the gelatin *foil* mentioned above; if this is not obtainable leaf may be used, but the diamond markings, which are highly strained, should be avoided. The squares are placed in watch-glasses or Petri dishes containing a few cubic centimetres of the following solutions: N/50 HCl, N/50 NaOH, N/1 $Na_2SO_4$, N/2 NaCl, N/2 $NH_4CNS$ and water. The squares should be held in a small forceps and immersed quickly and completely, without allowing air bubbles to adhere to them. The difference in swelling will be quite noticeable after one hour (when the gelatin placed in the thiocyanate solution is probably completely dispersed), although complete equilibrium is not attained for many hours. It must be remembered that the foil swells in all directions and that the increase in volume is, therefore, proportional to the *cube* of the side. The squares are best examined by holding the watch-glass 2″ or 3″ above a black background, when they appear

turbid, or of course by carefully pouring off the liquid.

*Purified Gelatin.*—The work described so far can be carried out with the raw material obtainable commercially. This always contains electrolytes, which it may be necessary to remove as far as possible, although it should be noted that the physical properties of the gelatin are sensibly affected by the prolonged washing which is required. A known quantity of the leaf is placed in a *weighed* tall beaker, capable of holding a volume of water equal to at least 15 times the weight of gelatin. Running water is then passed in near the bottom of the vessel and allowed to overflow for 48 hours. If an adequate supply of distilled water is available it may be used; failing this, tap-water may be employed, in which case washing must be completed with several changes of distilled water. To prevent the formation of mould a few fragments of camphor or thymol, wrapped in muslin, are added between the leaves, so as not to escape with the water.

Since gelatin imbibes something like 10 times its weight of water, sols of greater concentration cannot be made directly from the washed gelatin by warming to dispersion. To obtain them it is necessary either to dry the wet mass over $H_2SO_4$ or $CaCl_2$, or to evaporate the dilute sol to the required concentration at fairly low temperature, the concentration in either case being determined by weighing. The second procedure affects the sol perceptibly, especially if prolonged.

*Sols containing a Definite Amount per Volume.*—We have so far dealt only with sols and gels containing a definite percentage of gelatin *to* a given amount of water; in other words, with sols containing a definite amount of gelatin in a given *weight* of sol. The preparation of sols containing a definite amount of substance in a given *volume* is complicated chiefly

by the fact that sols are not liquid at the temperatures for which the usual measuring vessels are graduated, and the first point to decide is whether the sol is required to have a definite concentration at some particular temperature, say 35° for viscosity measurements, or at some arbitrarily chosen lower temperature, at which it may be transformed into gel. In the former case the flask to be used should be filled with water at the standard temperature and then placed in a water bath and warmed to the temperature selected; a fresh mark should be placed at the level reached by the water. The volume to this mark is calculated from the ratio of the specific volumes of water at the two temperatures selected; for 15° and 35° C. respectively these are, for instance, 1·00085 and 1·00586, so that the volume of, say, 500 c.c. measured at 15° will be

$$\frac{500 \times 1{\cdot}00586}{1{\cdot}00085} = 502{\cdot}5 \text{ c.c. at } 35°,$$

which figure is noted and the gelatin content calculated on it. Since it is inconvenient to soak and disperse the leaf in a long-necked flask, this should be done in a beaker with about 75 or 80 per cent. of the total volume of water required, the more concentrated sol thus obtained poured into the flask, which is placed in a thermostat at the required temperature, and the beaker washed out with successive small portions of warm water, which are transferred to the flask until the mark is reached. The contents of the flask, of course, require thorough mixing before use.

Commercial leaf contains a considerable amount of moisture, rarely less than 10 per cent., which must be taken into account. It can be removed almost entirely by drying at 100° to constant weight (note that gelatin takes up moisture from the air even during the time required for weighing), which treatment, however, affects the properties of the material

very considerably. It should, therefore, be applied only to a small sample, the rest of the material being kept in an airtight receptacle from the time at which the sample has been taken, so that its moisture content remains constant. When making up sols to a given concentration per volume, this should, of course, be calculated on the weight of *dry gelatin.*

It should be remembered that sols made by diluting a more concentrated sol differ slightly in their physical properties from sols produced by dispersing the gelatin at once in the total water required. To obtain comparable results it is again necessary to observe the rigid uniformity of procedure which has already been insisted on, *i.e.*, to use the same percentage for diluting, to have the added water at the same temperature as the sol, etc.

If *powdered* gelatin (the usual brands of which are, however, markedly less "hard" than the best brands of leaf) can be used, the procedure is simpler, since there is no difficulty in carrying out soaking and dispersion in the measuring flask itself. The latter should be about half filled with water by means of a long (thistle) funnel, so that the neck remains quite dry. The powdered gelatin is then poured in, in small portions and in *a thin stream, through a wide-necked funnel,* and the flask shaken frequently to cause the powder to sink without the formation of lumps. On no account must the powder be placed in the dry flask first. When the whole of the powder is submerged further water is added to within about 5 c.c. of the mark giving the volume at 15° C. (this refers to a 500-c.c. flask ; for other sizes the margin should be in proportion), and the necessary time allowed for swelling. The flask is then placed in the water bath, and the volume is made up to the mark giving the volume at the working temperature which has been fixed upon. Careful mixing before use is also required in this case, since the gelatin does not

diffuse perceptibly during dispersion, so that a concentrated layer of it rests on the bottom.

## LITERATURE.

A very complete Study of "Vapour Pressure, etc., of Gelatin-Water Systems," by K. Gericke, *Koll.-Zeitschr.*, XVII., 78 (1915); "Influence of Neutral Salts on Viscosity and Swelling," J. Loeb, *Journ. of Biol. Chem.*, 34, 77, 345 (1918).

## CHAPTER VII.

# EGG ALBUMIN SOL.

THE only commercial raw material is dried egg albumin, and the beginner should carry out the experiments described below with a sol made from it; although its use is open to objections, the results obtainable correspond sufficiently closely to those recorded in the literature for "natural" albumin.

Crush 15 gm. of dried egg albumin coarsely and introduce in small portions, with stirring, into 100 c.c. of water. The albumin at first adheres to the walls of the vessel with great tenacity, but is easily detached as imbibition proceeds. The sol should be stirred from time to time and lumps broken up until dispersion is complete. The sol is turbid, with a varying small fraction of insoluble matter, which does not settle even on prolonged standing. It must be filtered, preferably overnight, through asbestos in the manner described on p. 12; filtration through paper is extremely tedious and involves considerable loss. The filtrate from asbestos is a yellowish liquid, opalescent, but quite sufficiently clear in moderate thickness, say in test tubes 15 or 18 mm. diameter, to allow even incipient precipitation to be noticed easily. Albumin sols are very liable to undergo decomposition and should be used quite fresh; in warm weather a trace of thymol may be added to the mixture before filtration without affecting the properties of the sol.

*Heat Coagulation.*—Place a test tube containing about 10 c.c. of sol in a small water bath and heat slowly, stirring constantly with a thermometer. Note the temperature at which the sol begins to turn

white and opaque. Remove the test tube from the bath, add water and break up the coagulum, to show that it does not disperse again, *i.e.*, that the heat coagulation is *irreversible*.

*Irreversible Change by Adsorption.*—Albumin is readily adsorbed at the interface between sol and another liquid, and becomes insoluble in the process. This is easily demonstrated by placing in a test tube 10 c.c. of sol, adding 1 c.c. of some organic liquid heavier than the sol, *e.g.*, chloroform or carbon tetrachloride, and shaking vigorously, so that added liquid is broken up into small drops. These sink to the bottom and remain *perfectly separate*, which shows the formation of a film preventing their coalescence and evidently insoluble in the sol, as no change takes place even on standing for some time. To demonstrate that the adsorbed film is also insoluble in water, pour off the sol and replace by water; no coalescence occurs even then.

*Salting-out and the Hofmeister Series of Anions.*—It will be sufficient to try a few of the more characteristic salts of the series by adding the dry salts to the same volume of sol, so as to keep the albumin concentration approximately constant. The molar concentrations necessary to produce immediate turbidity in "natural" albumin sols (*i.e.*, sols containing, like ours, the other constituents of egg-white) are given below, as well as the amounts of the most readily obtainable salts required to produce these concentrations in 10 c.c. volume:—

| | M. per litre. | Gm. in 10 cc. of solution. |
|---|---|---|
| Na citrate . | 0·56 | 1·647 crystallized neutral sodium citrate. |
| $Na_2SO_4$ . | 0·80 | 2·577 crystallized sodium sulphate. |
| $NaCH_3.CO_2$ | 1·69 | 2·298 crystallized sodium acetate. |
| $NH_4CNS$ . | — | Ammonium thiocyanate to saturation. |

Place the coarsely powdered salts in flasks with a mark at 10 c.c., or, if these are not available, in test tubes 15 or 18 mm. diameter which have been provided with a mark at that volume. Place the flasks or test tubes in a water bath kept at about 35° and dissolve the salts gradually by slowly reversing the tubes at intervals ; they must not be shaken, as the formation of froth is to be avoided. Watch the appearance as solution proceeds and note that a *marked turbidity* appears only when the whole of the salt has gone into solution, except with thiocyanate, which does not salt out even in saturated solution.

Dilute the turbid sols with an equal volume of water, and note that they become clear, *i.e.*, the salting out is reversible.

*Reversal of the Hofmeister Series in Acid Sols.*—Acidify 20 c.c. of sol by adding 1 c.c. of normal hydrochloric acid. Place in one test tube the same quantity of sodium sulphate (2·577 gm.) as used above, and in another 3 gm. of ammonium thiocyanate, fill to the 10 c.c. mark with the acid sol, and dissolve the salts gradually. No precipitate is formed in the sol containing the sulphate, while the sol containing thiocyanate becomes turbid and eventually clots completely.

*Precipitation by Salts of the Heavy Metals.*—Prepare some ·2N solution of copper sulphate (say 12·480 gm. of the crystallized salt in 50 c.c. of solution). Add from a burette a few drops of this solution to 10 c.c. of sol ; a heavy greenish coagulum forms immediately. Continue to add copper sulphate solution, with occasional stirring ; the precipitate re-dissolves and has disappeared when 10 c.c. of solution has been added, *i.e.*, when the mixture is normal in respect of copper sulphate. Now add sufficient powdered copper sulphate to saturate the 20 c.c. (about 5·6 gm.) and dissolve ; a second

precipitation begins when the solution has become saturated.

To show that coagulation by salts of heavy metals is *irreversible*, repeat the experiment as far as adding a few drops of copper sulphate solution to 10 c.c. of sol, then dilute with water, and note that the coagulum does not dissolve.

The student desirous of working with pure albumin will do well to practise the usual methods of purification in the first instance with dried albumin. The methods are based on the fact that the constituents of white of egg other than albumin, viz., globulin, ovomucoid, etc., are salted out by lower concentrations of ammonium sulphate than is albumin. Disperse 15 gm. of dried egg albumin in 100 c.c. of water, as described, but do not filter the sol. Add in small portions sufficient finely powdered pure ammonium sulphate to produce a *half-saturated* solution; 38 to 39 gm. is required. Each addition should be made only after the previous one has dissolved. A white coagulum forms and is removed by filtration through a folded paper filter. The filtrate contains the albumin dispersed in half-saturated ammonium sulphate solution. The salt can now be removed by dialysis in parchment, or, better, collodion against running water, and a moderately pure albumin sol obtained. The usual method is, however, to precipitate the albumin by saturating the solution with ammonium sulphate, a further 38 to 39 gm. being required for every 100 c.c. of filtrate. A thick coagulum of albumin forms, which is filtered overnight and allowed to drain as far as possible. The residue, which always contains a considerable amount of mother liquor, is then dissolved in the smallest volume of water which will give a clear sol, and dialysed as explained above to remove ammonium sulphate.

The same method is applied to fresh white of eggs.

About 28 to 30 c.c. of white can be obtained from average fowls' eggs; this contains about 10 per cent. of albumin. The total protein content is about 12·2 per cent., the difference being accounted for by globulin and mucoid. The egg-white is beaten up with *an equal volume* of saturated ammonium sulphate solution, which produces half-saturation in the mixture and precipitates the latter constituents. The coagulum is filtered off and the filtrate saturated with ammonium sulphate to precipitate the albumin, which is filtered off and dissolved in a small volume of water. This sol is again precipitated by saturation with ammonium sulphate, and the previous operations repeated; several re-precipitations are required to obtain pure albumin. The last coagulum is dissolved in a small volume of water and dialysed to remove the sulphate. The losses are fairly considerable, and the albumin content of the sol finally obtained after dialysis will be between 2 and 2·5 gm. of albumin for every 30 c.c. of white used originally.

Although the general student will hardly have occasion to use it, the classical method of making "crystallized albumin" is here given. It may be tried with the white of two or three eggs, which should be *perfectly fresh.* The volume of egg-white *is measured* and an exactly equal volume of saturated ammonium sulphate solution added to it in small portions at a time, the mixture being vigorously beaten with an egg-beater after each addition until the whole has been reduced to a stiff froth. This is allowed to stand overnight, and is then filtered to remove the coagulum of globulin, etc. Ten per cent. acetic acid, *i.e.*, glacial acetic acid diluted to 10 times its volume, is then added to the filtrate from a burette, a single drop at a time, with gentle stirring to re-dissolve the precipitate formed locally before a further drop is added. This is continued until the solution becomes *permanently turbid*—the exact

degree of turbidity can only be found by practice, but must amount to something more than mere opalescence. When this point has been reached, 1 *c.c. of acid for every* 100 *c.c of solution is added.* A copious precipitate forms, which, on standing and occasional gentle shaking, becomes (micro-)crystalline after five or six hours ; to obtain the full yield it should, however, be allowed to stand for 24 hours. The precipitate is filtered off and dissolved in a small volume of water ; the solution is then dialysed, or, if further purification is desired, it is again precipitated. This is done by dissolving the coagulum from the filter in the smallest possible volume of water, acidifying with a few drops of 10 per cent. acetic acid, and then adding concentrated ammonium sulphate until a slight permanent turbidity results. After 24 hours' standing the bulk of albumin has been re-precipitated.

The beginner will find the exact degree of turbidity required somewhat difficult to judge and must be prepared for disappointment. In dialysing albumin sols remember what has been said on page 27 regarding sols which exert an appreciable osmotic pressure and use suitable arrangements.

### Literature.

This is too voluminous to allow of being summarised. Students must consult the text-books on Proteins or those of Biochemistry.

## CHAPTER VIII.

# EMULSIONS.

BOTH as regards methods of preparation and properties these fall into two classes, which are best studied separately: the pure oil-water emulsions, in which no solute is present in the water, and the concentrated emulsions, which can be produced only by adding to the water phase certain substances which greatly lower its surface tension and occasionally possess other properties as well.

*Pure Oil-Water Emulsions.*—These are most conveniently prepared by the following method: 0·1 c.c. of the oil (which may be a paraffin oil of low viscosity, oleic acid, or generally any other liquid immiscible with water, but soluble in alcohol) is dissolved in 10 c.c. of alcohol or acetone. This solution is blown from a pipette into one litre of water; the water is well agitated before immersing the pipette, the point of which should be 10 to 15 cm. below the surface. The resulting emulsion should show a bluish tinge in reflected light (particularly well marked with oleic acid), and be practically clear in transmitted light.

The emulsion should be examined with a dark-ground condenser and the sign of the charge determined in the cataphoresis apparatus. The coagulation by HCl should be watched under the microscope as the phenomenon, viz., coalescence of discharged particles to bigger ones, with decreasing amplitude of Brownian movement, is slow and more easily followed than with suspensoids, with the behaviour of which it otherwise agrees.

Electrolyte coagulation should be tried with HCl and with, say, $CaCl_2$ and $Al_2(SO_4)_3$; salts of univalent cations act only in very great concentrations. The effect of the coagulant shows itself macroscopically by the disappearance of the bluish opalescence, the emulsion becoming whitish and turbid instead. Samples should be taken at intervals and examined microscopically (ordinary illumination, using sub-stage condenser and a fairly small diaphragm, magnification about 600 diameters), when it will be found that globules about $3\mu$ diameter gradually take the place of smaller ones, this being the size at which Brownian movement becomes so sluggish that further collisions between globules, and therefore formation of larger ones, practically cease to occur.

The emulsions to which sufficient coagulant has been added gradually clear from the bottom upwards, provided the " oil " has a density lower than that of water. The rate of clearing should be measured at convenient intervals, 24 or 48 hours, according to the difference in density, and the size of the globules calculated from Stokes's formula (*determine density of oil to three decimals*).

*Concentrated Emulsions.*—To prepare these it is necessary to lower the surface tension of the aqueous phase, the most convenient agent for the purpose being a soap. Either a soap solution may be used, the preparation of which will be described below, or the soap may be actually produced in the process of emulsification. This method, which of course is applicable only to oils which are glycerides, consists in shaking up the oil with a dilute solution of caustic soda, N/50 to N/100 being suitable concentrations. Small quantities may be prepared in test tubes; pour 10 c.c. of the NaOH solution into a test tube of 25 to 30 c.c. capacity, then add ordinary olive or cotton-seed oil in lots of 1 c.c., close the test tube

with the thumb and shake vigorously after each addition. The emulsion becomes a pure white (*why ?*), and after the addition of about 10 c.c. of oil the viscosity increases so much that the dispersion of further oil becomes difficult. Larger quantities may be prepared in the same way in any shaking apparatus which may be available; in this case, too, the oil should be gradually added in small portions.

The oil in emulsions thus prepared gradually rises, a sharp boundary forming between the concentrated emulsion at the top and the dispersion medium, which is turbid owing to the presence of soap and very fine particles. This rise continues until the oil globules are in closest packing; as they are not of uniform size, no exact figure can be given for the percentage of disperse phase, but it will be found to be 70 per cent. or over. The volume ratio can be determined, with small errors due to contraction, etc., in the following way: a burette is filled to the lowest mark (*i.e.*, the one bearing the highest number) with dilute hydrochloric acid. The emulsion is then poured into the burette, the volume noted, the burette closed with the thumb, and emulsion and acid thoroughly mixed. The oil separates and rises; any small globules which may remain separated from the main bulk must be made to unite with it by tapping and inclining the burette. The volume of oil is then read off and the volume of continuous phase obtained by difference.

When mineral oils are to be emulsified the procedure described is not applicable, but soap solution must be employed. Ammonium oleate is extremely efficacious, but is not obtainable commercially, and sodium oleate (olive oil or Marseilles soap) will generally have to be used. It is cut into fine shavings, which are allowed to dry in air for three or four days, and 10 gm. of the air-dried material dissolved in one litre of distilled water, at 30° to

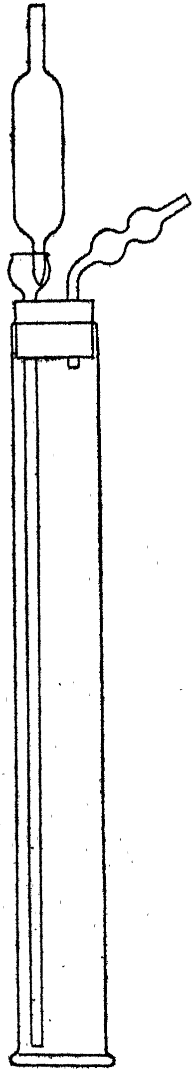


FIG. 10.

40° C. The solution is allowed to stand in the cold for 24 hours and then filtered twice through the same filter of fairly open paper.

Emulsification may be accomplished by shaking, as described above. If no shaking device is available, fair quantities may be prepared in the apparatus shown in Fig. 10, which may be made up from vessels to be found in the laboratory. A tall cylinder is closed by a rubber stopper with two perforations. A thistle funnel, having a tube 3 to 4 mm. diameter, reaching to within 3 or 4 mm. of the bottom of the cylinder, passes through one of the perforations; a ball tube, with two or three balls, through the other. A large pipette —50 to 100 c.c.—with its lower end drawn to a capillary point, is suspended above the thistle funnel so that the point touches the wall of the funnel. The point is made so fine that 50 c.c. of oil of low viscosity, like the paraffins used in lamps, takes 25 to 30 minutes to empty. If the flow is found too rapid it may be reduced by fitting a short length of rubber tubing, provided with a screw clip, to the upper end of the pipette.

The apparatus is used as follows: The stopper is removed and a known volume of soap solution poured into the cylinder; it should not exceed one-third of the total

volume. A few drops of the oil to be emulsified are then poured down the funnel and the latter rotated slowly, so that the whole of the tube is wetted by oil. The stopper is then replaced, the pipette filled with oil suspended as explained above, and the ball tube connected to the filter pump. The latter should be so adjusted that the air issues in a uniform string of separate bubbles at the bottom of the funnel tube. When the pump is working properly, the clip at the top of the pipette is opened to the required extent, and the apparatus then requires no further attention. The oil, which runs down the tube in a very thin film, is broken up by the air bubbles when passing out at the lower edge of the tube, and thorough emulsification takes place. Frothing is rather marked at the beginning, but subsides after a little oil has been emulsified, and the ball tube prevents froth from being drawn into the suction tube to any extent.

The emulsions made with soap solution separate a "cream," like those prepared with caustic soda, and the same methods may be used for determining the volume ratio.

Emulsions which do not separate, whatever the volume ratio, can be made from oils which have the same density as the dispersion medium. The simplest way is to prepare suitable mixtures of either olive oil, cotton-seed oil, or lamp paraffin with carbon tetrachloride (density at 0° 1·632). The ratio may be approximately calculated from this and the density of the oil; as, however, the co-efficients of expansion of the aqueous dispersion medium and the mixture of oil and $CCl_4$ differ widely, exact equality can only be secured by experiment *at a definite temperature*. For this purpose the—approximate—mixture and a small beaker filled with the soap solution are placed in the thermostat, a 1 c.c. pipette filled with the former, and slowly blown out

under the surface of the soap solution, so that a single drop is formed, which can easily be detached from the pipette. According as this drop rises or sinks, more $CCl_4$ or more oil is added to the mixture, until the drop remains practically stationary for a few minutes. Emulsions of this kind are especially suitable for viscosity measurements (which see).

### LITERATURE.

For recent papers, see article "Emulsions" in Second Report of British Association Committee on Colloid Chemistry, 1918, p. 20.

## CHAPTER IX.

## ULTRA-FILTRATION.

THE name was given by H. Bechhold to a method of separating the disperse phase of sols from the dispersion medium by means of filtration under pressure through porous membranes impregnated with gels, the permeability of which may be varied within wide limits. As considerable pressures may have to be used metal apparatus is essential, which limits the applicability of the method to some extent. An apparatus suitable for sols containing a very small amount of solid only (as is the case with most suspensoid sols) is illustrated in Fig. 11. The filtering membrane rests on a perforated metal disc *a*, which is clamped between the body *b* of the filter and the slightly conical bottom *c* and rests on six radial ribs in the latter. The branch *d*, closed by a screw cap, serves for filling the filter, and the necessary pressure is generated by a bicycle tyre pump connected to the valve *e*. The joint between the vessel and the cover is made tight by a rubber ring cemented to the spigot on the former with marine glue or Chatterton's compound. To prepare the filter for use, the cover with the perforated metal plate is removed, the membrane placed carefully on the latter; the cover is then replaced and the two nuts tightened. The filter is then charged through the large inlet, the cap replaced and tightened, and pressure generated by means of the bicycle pump. The filter should not be more than about half full, so as to leave a sufficient air space, as otherwise the

pressure falls too rapidly and the apparatus requires continuous attention and pumping. The pressure to be used depends on the denseness of the membrane; two or three atmospheres (30 to 45 lbs. per square inch) will generally be sufficient, but the

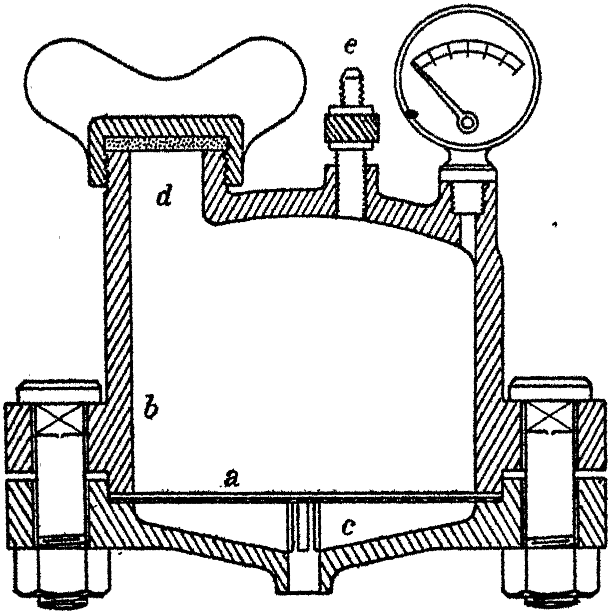



FIG. 11.

apparatus should be strong enough for a maximum working pressure of five atmospheres, *i.e.*, it should be tested with eight atmospheres, as this adds very little to the cost. The apparatus is supported on a tripod stand, and the beaker or flask for the filtrate placed below it.

The membranes are made from circles of filter paper impregnated with either acetic acid collodion

or gelatin. A hard filter paper, such as used for vacuum filtration on Buchner funnels, must be employed; brands equivalent to Schleicher and Schuell's Nos. 575 or 602 are suitable.

Collodion membranes are more convenient than gelatin ones; their permeability, *i.e.*, the average size of the particles which are just retained, varies with the concentration of the collodion. As it is difficult, without experience, to foretell what concentration will answer in any given case, a range of filters should be prepared impregnated with, say, 1, 2, 3, 5, 7 and 10 per cent. collodion, *i.e.*, sols of collodion cotton containing 1, 2, etc., gm. of cotton in 100 c.c. of sol, the solvent being glacial acetic acid. The preparation of these sols has been fully described under "Dialysis," p. 24.

If a number of filters are prepared with sols of various concentrations, the latter *should be marked in pencil on the disc before impregnation.* The sol is poured into a small dish—a *porcelain* developing dish does very well,—a filter paper seized in a forceps near the edge, within the width which will eventually be covered by the rubber joint ring, and slowly immersed in the sol under a very acute angle with its surface. Care must be taken not to trap any air bubbles underneath the paper and to have it uniformly penetrated by the sol; this is readily seen by the paper becoming translucent, like oiled paper, while spots not penetrated by collodion remain opaque and white. The thoroughly impregnated disc is then slowly withdrawn from the liquid and held vertically above it to allow the excess to drain off; it should be turned to and fro in its own plane, as otherwise a thick ridge is formed at the bottom, which may prevent a good airtight joint being made when the disc is clamped in the apparatus. The discs are then submerged in water, which is constantly changed until all acetic acid has been washed

ıut, and may then be kept indefinitely in water aturated with chloroform or camphor, to prevent he formation of mould.

Gelatin sols containing from 2 to 10 per cent. may e used instead of collodion, the sols being prepared n the usual way. The vessel containing the sol luring impregnation must be placed in a water bath, ınd the temperature chosen should be maintained onstant *and adhered to throughout,* as otherwise ilters made even with the same concentration will ary considerably. The discs are impregnated and lrained as described, during which time the sol sets o gel; they are then hardened in a cold solution of ormaldehyde, 2 to 4 per cent., which is placed in a efrigerator for 24 hours. The discs are then rinsed n water and can be kept under water saturated with hloroform. *If either collodion or gelatin ultra-filters re allowed to dry, even partially, they become useless.*

Two per cent. collodion filters should give a colourless filtrate with Prussian blue sol (prepared as lescribed on p. 34), while 3 to 4 per cent. filters hould retain practically the whole of the disperse hase in ordinary gold sols (reduced by formaldehyde r tannin).

The use of special apparatus and the consequent ontact with metal can be avoided by adopting either of the following methods of making ultrailters, which are due to Wo. Ostwald. The first one urnishes membranes suitable for use with the filter ump, while the second one produces "spontaneous" ıltra-filters, *i.e.*, membranes of sufficient permeability o allow liquid to pass simply by hydrostatic pressure.

1. *Filters for Use with Vacuum.*—The collodion ısed has the following composition: collodion otton, 2 gm.; alcohol, 14 c.c.; ether, 84 c.c.; or the commercial "Collodion P.B." or "Collodion, methylated" may be used.

For preparing conical funnels, a circle of ordinary

rough filter paper is folded twice in the usual way and placed in a well-fitting, smooth glass funnel. To ensure perfect fit it may sometimes be advisable to make one fold only at first, to place the paper in the funnel, and to make the second fold when good contact all round has been secured by careful smoothing. The filter thus prepared is filled with collodion up to the edge; when this has penetrated the paper over the entire surface, the excess is emptied, the filter being slowly turned while this is being done. Turning is continued while the collodion dries superficially (the time required depends on the room temperature and the desired permeability, and may be from three to six minutes); when it no longer sticks to the finger on being touched *lightly*, the funnel is placed in distilled water. The filter is ready for use after about 15 minutes' immersion, but may be kept under water indefinitely provided chloroform or camphor is added.

The same method may be adopted for preparing Buchner funnels, but in this case a joint must be made between the edge of the paper and the perforated plate *before* impregnation, as otherwise the collodion gets under the paper. A solution of 2 gm. of white crepe rubber in 100 c.c. of petroleum ether is used for the purpose. The funnel is inclined under an angle of 45° and a few cubic centimetres of the rubber sol poured down the side, care being taken that it does not reach the perforations. By turning the funnel round the sol is distributed to form a band round the perforated area, and while this is still "tacky" the circle of filter paper is placed in position and squeezed down all round. After a few minutes' drying a second rubber band is produced in exactly the same way, and when this has dried the paper is impregnated with collodion, as described above. When the collodion has dried to nearly the required extent a *third* rubber joint is made,

and the funnel placed in distilled water, as before described.

2. *Spontaneous Filters.*—The collodion for these contains 4 gm. of collodion cotton to 12 c.c. of alcohol and 84 c.c. of ether. A circle of ordinary rough filter paper is folded twice in the usual way, placed in a well-fitting smooth funnel, and *thoroughly wetted with distilled water.* Any excess is poured off or allowed to drain through ; if a little remains in the point of the filter it must be removed with a twisted spill of filter paper. The funnel is then partly filled with collodion, which is spread uniformly by inclining and turning, the excess poured off, and the collodion allowed to dry for four to five minutes, after which a second layer of collodion is poured in the same way. When this has dried a few minutes the filter is ready for use. A properly made filter of this kind should give a *colourless* filtrate with a gold sol made by reduction with formaldehyde.

Buchner funnels may likewise be used, no rubber joint being necessary in this case. The paper is thoroughly wetted with distilled water and placed flat on the perforated plate. Sufficient collodion is then poured on to cover the whole of the paper, and the excess poured off, leaving, however, a remnant of two or three cubic centimetres, which is carefully distributed round the edge of the paper by inclining the funnel about 45° and turning it continuously until the collodion no longer flows. A second lot of collodion is poured in exactly the same way after the first one has dried to the desired extent, and the filter is ready for use when this is sufficiently dry. Particular attention must be paid to getting a sufficient rim of collodion round the edge of the paper, as this makes the joint and prevents the liquid from escaping underneath the paper.

An extremely convenient method of making small ultra-filters consists in the use of the seamless

extraction thimbles, which can be obtained in a variety of sizes. If apparatus for using them with vacuum is available, they may be impregnated dry, as described under (1); otherwise it is more convenient to impregnate them wet and use them as spontaneous filters by placing them in a loosely-fitting cylindrical funnel.

## CHAPTER X.

# OPTICAL METHODS OF EXAMINATION.

THE simplest and most sensitive method of showing the presence of disperse matter in a liquid is examination by the Tyndall cone, *i.e.*, a narrow beam of intense light projected through the liquid and viewed at right angles to the direction of the axis of the beam. The liquid to be examined is placed in a prismatic cell; the small cemented specimen cells supplied by most makers of apparatus are suitable. If possible, cells cemented with dichromate-gelatin should be chosen, as they can be used both for aqueous solutions and organic solvents. One face of the cell is covered with black velvet, or, better still, the cell is placed in a small wooden box, provided with two circular openings (Fig. 12) at right angles to each other and lined with black velvet or painted a dead black with Indian ink. The light from a small hand-regulated arc lamp, Nernst lamp with horseshoe filament, or a tungsten arc ("point o' light lamp"), is projected through the cell by means of a lens so placed that the focus falls about the middle of the cell, opposite the second opening, through which the path of the beam is viewed. All light should be screened. If particles are present the beam is visible; when the disperse phase is colourless (*e.g.*, mastic suspension) the cone shows a bluish tinge; when it is coloured the beam may show a colour different from that of the liquid viewed in transmitted light (*e.g.*, red gold sols, in which the cone shows green). It must be remembered

that even true solutions of substances of high molecular weight, *e.g.*, cane sugar, show the cone, and that it is not entirely absent even in filtered distilled water. Water freshly ultra-filtered and collected with due precautions against contamination by dust is nearly "optically void," *i.e.*, the cone is invisible.

By placing a suitable analyser, say a Nicoll prism mounted in a collar permitting it to be rotated, in the opening A, the light emitted by the cone can be shown to be polarized; if the Nicoll is rotated the intensity of the cone varies, becoming a minimum in

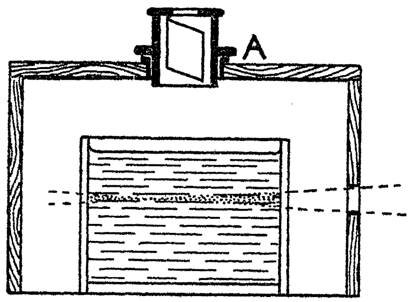



FIG. 12.

two positions of the prism at 180° from each other. Complete extinction occurs only with a disperse phase consisting of a non-conductor (mastic suspension).

*Ultra-microscopic and Dark-ground Examination.*—The "slit" ultra-microscope and the cardioid condenser require large arc lamps and special wiring, and are beyond the scope of this book; those in a position to use them will obtain all necessary instructions from the makers. Real ultra-microscopic illumination is provided by the Jentzsch ultra-condenser, a section through which, showing the path of the rays, is shown in Fig. 13. It has the advantage of requiring

only a 4 to 5 ampere hand-regulated arc lamp, of holding a comparatively large volume of liquid, so that adsorption effects are minimized, and of being very easily centred. The optical part is cemented into a cylindrical metal casing, which is closed by a metal cover provided with bayonet joint and a central quartz window for observation. The ultra-condenser is placed on the stage of the microscope so that the spigot on its lower side fits the opening in the former—the ordinary condenser being, of course, removed and the plane mirror used for illumination. The dimensions of the ultra-condenser do not permit the use of objectives of shorter focal length than 6 mm. (or $\frac{1}{4}''$), but, as the images are not geometrical, there is no limit to the eyepiece magnification permissible, and the highest power eyepiece available may be used.

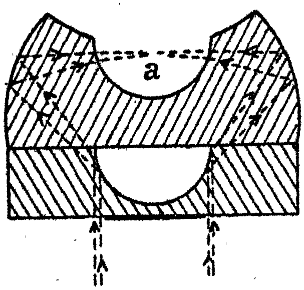



FIG. 13.

The condenser is filled with the liquid to be examined by means of the inlet and outlet branches provided on the cover, care being taken not to leave an air bubble at the top of the liquid under the quartz cover. The light from the arc lamp, which should be provided with a lens giving a nearly parallel beam, is then directed on the plane mirror, which it should fill completely and uniformly, and the condenser placed in position. The light is now centred, using the $\frac{1}{4}''$ objective and a *low power* eyepiece, by adjusting the mirror until the brightly illuminated spot is exactly in the centre of the field. The low-power eyepiece is then replaced by the highest power available; Zeiss's No. 18 compensating eyepiece, or an equivalent, is suitable. The

most highly illuminated layer will be easily found by focussing up and down, and, as this layer is at some distance from any boundary surface, the Brownian movement will be seen in great perfection. The large diffraction rings which appear and disappear round many particles indicate, of course, vertical movement out of the focal plane.

Coagulation of sols can be very conveniently studied with this condenser by running in an electrolyte solution through one of the branches on the cover, or by adding a small amount of coagulant to the sol before it is filled into the apparatus. After use the condenser must be carefully washed with distilled water and thoroughly dried with linen free from grease. This applies equally to the metal parts in contact with the liquid.

If the ultra-condenser is not available, the presence of at least coarser ultra-microscopic particles can be detected by means of one of the numerous dark-ground condensers. Typical forms of this apparatus are the Zeiss "Paraboloid" condenser, the Reichert "Table" condenser, and the Jentzsch "Concentric" condenser, which latter, like the Jentzsch ultra-condenser, is now made in this country. The methods of using and centring are slightly different with the different types, and are generally adequately described in the makers' pamphlets. Since they all depend on total reflection at the cover glass, slides of the thickness prescribed by the makers must be used in all cases. Both slides and cover glasses must be carefully cleaned in the following manner. They are washed in hot dichromate-sulphuric acid mixture for five to ten minutes and then rinsed thoroughly with distilled water. The slides or cover glasses are then seized, one by one, with a spring forceps and, after draining off the bulk of the water, placed in strong alcohol, in which they are kept until required. Immediately

before use the slide is withdrawn from the alcohol by seizing one corner with a spring forceps, and the adhering alcohol burnt off over a spirit lamp or Bunsen burner. As soon as the slide has cooled it is placed on the condenser, ample cedar oil being used, as explained in the descriptive pamphlets. The cover glasses may be treated in the same way, provided they do not crack too frequently; if this should be the case, the alcohol may simply be evaporated at a sufficient distance from the flame to prevent ignition. Before the cover glass is made ready a large drop of sol, free from any air bubble, should be placed on the centre of the slide, and the cover glass dropped gently on it immediately it has cooled. *The essential point of the method described is that slides and cover glasses are not touched with the fingers or with any textile material, as this renders them entirely useless for ultra-microscopic work.*

The layer of liquid between cover glass and slide is, of course, of very slight depth, and careful focussing on its central portion is necessary to observe particles moving freely. Many particles will always be found, by suitable focussing, to have adhered to the two glass surfaces. Electrolyte coagulation can be observed, though in a somewhat rough fashion, by placing a drop of solution on the edge of the cover glass, so that it can diffuse into the bulk of liquid. The most convenient objects for becoming familiar with the use of the apparatus are comparatively coarse systems, especially mastic or gamboge suspensions.

### LITERATURE.

Full information on the various types of condensers is to be found in the pamphlets issued by the makers (Zeiss, Leitz and Chas. Baker). Photometric investigation on Tyndall cone, connection between size of particles and luminosity, etc., by W. Mecklenburg, *Koll.-Zeitschr.*, XIV., 172 (1914); XV., 149 (1914); XVI., 97 (1915).

## CHAPTER XI.

## CATAPHORESIS.

A SIMPLE apparatus, suitable for practice and preliminary work, may be made up from glass parts available in every laboratory in the manner illustrated in Fig. 14. A U-tube, about 250 mm. long, provided with an inlet tube at the lowest point of the bend, is supported in a suitable stand. The inlet tube is connected by a rubber tube, about 350 mm. long, to a funnel capable of holding about 75 c.c. The tube is fitted with a screw clip or with one of the patent clips provided with a catch, which allows it to be left fully opened, near the end of the inlet tube.

Two electrodes are inserted in the tops of the limbs, consisting of foil rolled into a cylinder, the diameter of which should be about 2 mm. less than that of the tube. Platinum is, of course, the best material, failing which, silver; even cylindrical solid carbon electrodes may be employed, but small particles are liable to become detached from the latter during use. The electrodes are fixed to stout wires, which are best mounted in a strip of ebonite, acting also as distance piece, and provided with terminals.

The apparatus is charged in the following manner. The clip is opened and the sol to be examined poured into the funnel, the latter being held so that its edge is about 10 mm. above the bottom of the bend. The liquid should just reach the latter; the funnel is then lowered and again raised to the original level, to drive out any air which may have been trapped

in the rubber tube, and the cock closed, with the sol standing just at the bottom of the U-tube. Distilled water is now poured into the latter so as to fill the limbs to about half their height. The funnel is then raised *until the level of the liquid in it is about* 1 *mm. below that of the water in the limbs, and the cock opened full bore.* The funnel is now very slowly raised, the sol flows into the U-tube, and the level of the water in the limbs rises correspondingly. The funnel must be raised at the same rate, *i.e.*, the level of the sol in the funnel should never be more than 1 or 2 mm. above the water level in the limbs. If this is done properly, the sol rises in the U without mixing with the water, and eventually shows a sharp boundary in both limbs. If the funnel is raised too rapidly, or if the cock is not fully opened, the sol issues in a jet, impinges on the upper wall of the U-bend, and rises unequally in the limbs, without filling them completely and without forming the necessary sharp boundary surface against the water. While it is quite easy to fill the tube properly after a little practice, the beginner will find the pro-

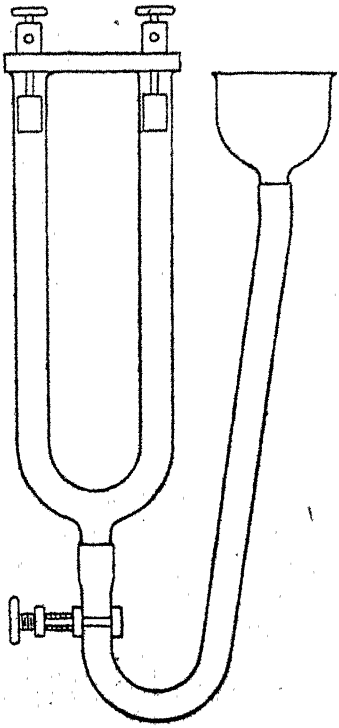


FIG. 14.

cedure much facilitated by a loose plug of carefully washed cotton or glass wool, placed in the inlet tube at its junction with the bend. This checks and distributes the admission of the sol and prevents its issuing in a jet.

Sufficient sol must, of course, be admitted to raise the water level in the limbs so far that the electrodes are covered completely. When this is the case they may be connected to the electric supply; the lighting supply may be used, of course with sufficiently insulated wires or flexible leads. With a voltage of 200 the gradient in a tube of the dimensions described above is about 5V/cm., so that a very distinct shifting of the boundary is noticeable after 10 minutes. The polarity of the electrodes must, of course, be determined, *e.g.*, with the "pole finding paper" obtainable for this purpose. Rough measurements of the rate of travel may be made by marking the original boundary and measuring the displacement (choosing whichever boundary is the sharper) after a definite time. The field strength is the voltage divided by the distance of the electrodes; the latter is somewhat uncertain, but the total distance in the axis of the tube, *i.e.*, twice the length of the straight limb, from the lower edge of the electrode, plus half the arithmetical mean of the internal and external circumference of the bend, may be taken as approximately correct.

For exact work a specially made apparatus is preferable, which incidentally avoids the use of rubber connections. A convenient form (after W. Nernst and A. Coehn) is illustrated in Fig. 15. It consists of a U-tube provided with two large cocks at the junctions of the straight limbs with the bend. An inlet tube, about 3 or 4 mm. diameter, leads into the lowest point of the latter, and is bent at right angles to the plane of the drawing, terminating at the top in a charging funnel of suitable

capacity. A scale of millimetres (*not cubic centimetres !*) may be etched on the limbs. The limbs are provided with electrodes such as described above.

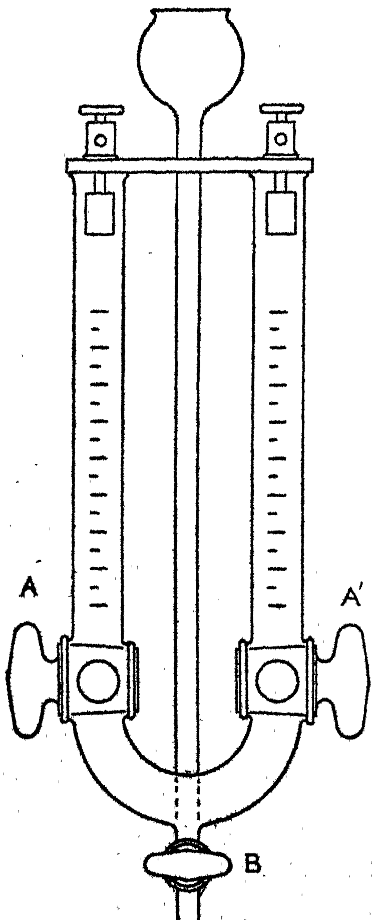



FIG. 15.

The apparatus is charged as follows. The funnel is filled with the sol to be examined, the cocks A and A′ opened, and then the cock B, until the sol just rises above the large cocks. B, and subsequently A and A′ also, are closed, and the small amount of sol in the limbs removed with spills of filter paper. The limbs are then filled to the same height with distilled water and the electrodes placed in position. The cocks A and A′ are now opened, and then B, which must be done very slowly and uniformly. The sol and the supernatant water in the limbs now rise; sol is admitted until the electrodes are submerged, when they may be connected to the supply. What has previously been

said regarding the electric gradient, of course, applies equally to this form of apparatus.

If measurements of the velocity of cataphoresis are made, the results are usually reduced to unit gradient, as stated. To give an example, the boundary travels to the anode, the displacement amounting to 22 mm. in 10 minutes. The velocity per second is accordingly $2{\cdot}2/600$ cm. $= 0{\cdot}00366 = 366 \times 10^{-5}$. With a voltage of 240 V and a distance of 24 cm. between the electrodes the gradient is $240/24 = 10$ V/cm. The velocity reduced to unit gradient is, therefore, $366/10 \times 10^{-5} = 36 \times 10^{-5}$, which is a normal value for the more highly dispersed gold sols.

*Microscopic Observation and Measurement of Cataphoresis.*—Any one of the "dark-ground" condensers described in the chapter on optical methods of examination may be employed. A slide must be provided with electrodes having parallel edges, between which the liquid is contained. The electrodes are two strips of metal foil; platinum is, of course, preferable, failing which silver may be used. The strips should be 3 mm. wide and about 35 to 40 mm. long for the standard microscope slide, $1'' \times 3''$. They are fastened parallel to each other and at right angles to the length of the slide, so that the distance between the *outside* edges is equal to the width of the cover glass to be used. A $\frac{7}{8}''$ cover will be found convenient, this making the distance between the outside edges of the strips about 22 mm., and the distance between the inside edges, *i.e.*, the distance between electrodes, about 16 mm.

The strips are fastened to the slide, which has previously been thoroughly cleaned in the manner already described, with Chatterton's compound (a preparation made for insulating purposes). A small piece of the preparation is warmed sufficiently and drawn out into a thin filament about 1 mm. diameter.

The slide and the two strips of foil are then placed on a warm metal surface and a piece of the filament about 25 mm. long laid on each strip, centrally as regards width, and at one end of the strip, so as to leave a length of 10 to 15 mm. clear. The strips, as soon as the filaments of compound have softened, are picked up with a forceps, inverted and placed parallel to each other on the slide the requisite distance apart (the position of the outside edges can be previously marked with a diamond or a drawing-pen). They should be dropped down into the correct position without subsequent shifting, to avoid smearing the slide with the compound. As soon as the strips are in position the slide is removed from the warm surface and placed on a clean piece of filter paper resting on a wood or glass table; the strips are then weighted by placing them on a second microscope slide and on this a 50-gm. weight. Sufficient time—from 10 to 20 minutes according to the temperature of the room—must be allowed for the complete hardening of the cement.

Electric connection to the electrodes may be made simply by pressing the wires down on the projecting ends of the electrodes, of course taking care to insulate the latter from the stage of the microscope by a piece of thin sheet rubber or the like. For repeated use it is, however, more convenient to solder leads of thin flexible cord to the ends of electrodes, the opposite ends being provided with terminals kept apart by a distance piece of ebonite. The flexible cords should be of sufficient length to allow the terminals to rest on the table, out of the way of the mirror, when the slide is in position on the stage of the microscope.

The slide is placed on the stage and optical connection made with the particular condenser used in the manner prescribed for it. The slide should, if possible, be clamped down to avoid accidental

shifting. A large drop of the liquid is then placed in the centre of the space between the electrodes; this should be of sufficient size to cover the field between the edges of the two strips, and make good contact with both, when the cover glass is put on. The microscope is then focussed on the central layer of liquid, so as to observe particles which are moving freely, and the current turned on. In view of the short distance between the electrodes a supply at 4 to 5 V is sufficient (say, from accumulators or dry cells). The velocity may be measured by means of an eyepiece micrometer and stop-watch. Release the latter when a particle under observation passes through one of the numbered divisions, and arrest the watch when it has travelled, say, through five divisions. The actual value of the micrometer reading must, of course, be known, or determined in the usual way with a stage micrometer. The potential gradient is: voltage at terminals/distance of electrodes in centimetres. To obtain the velocity of the particles in unit gradient, *i.e.*, one volt per centimetre, divide the velocity actually found by the gradient. For instance, a particle is found to travel five divisions of the scale in 32 seconds. Five divisions, with the particular objective and eyepiece used, correspond to, say, 0·24 mm. = 0·024 cm. = $24 \times 10^{-3}$ cm. The velocity per second is, therefore, $24/32 \times 10^{-3} = 75 \times 10^{-5}$ cm. With a voltage of four and a distance between the electrodes of 1·6 cm., the gradient is $4/1{\cdot}6 = 2{\cdot}5$ V/cm. To obtain the velocity in unit gradient, the figure found above must, therefore, be divided by 2·5, so that we finally obtain the velocity per second in a field of one volt per centimetre $= 75/2{\cdot}5 \times 10^{-5} = 30 \times 10^{-5}$ cm. This is a normal value for a metal sol.

The microscopic method is particularly convenient and rapid for determining the *sign* of the electric charge when only small quantities of the liquid

under examination are available. When using it for this purpose, *remember that the image is reversed*, so that, if the anode is on the right, negatively charged particles will travel to the left in the field of vision. Measurements, however, may be subject to fairly considerable errors unless a layer of particles is observed which moves freely and beyond the influence of the two glass surfaces. A cell designed to minimize the sources of error has recently been described by Th. Svedberg, a reference to which will be found in the literature given below.

### LITERATURE.

For the microscopic method generally, see A. Cotton, and H. Mouton, "Les ultramicroscopes, etc.," Paris (1906). For elimination of errors, Th. Svedberg and H. Andersen, *Koll.-Zeitschr.*, XXIV., 155 (1919).

## CHAPTER XII.

# ELECTROLYTE PRECIPITATION OF SUSPENSOID SOLS.

BEFORE starting experimental work the student should commit to memory a few typical figures for the concentrations of uni-, bi- and tri-valent ions which produce precipitation in suspensoid sols. The following are representative :—

| Sol. | Sign of charge. | Precipitation concentration in millimoles/litre. | | | | | |
|---|---|---|---|---|---|---|---|
| $As_2S_3$ . | Negative | NaCl | 51·0 | $CaCl_2$ | 0·65 | $AlCl_3$ | 0·09 |
| Pt . | ,, | NaCl | 2·5 | $BaCl_2$ | 0·06 | $AlCl_3$ | 0·01 |
| Mastic | ,, | NaCl | 1,000 | $CaCl_2$ | 25 | $AlCl_3$ | 0·2 |
| $Fe(OH)_3$ | Positive | NaCl | 9·25 | $K_2SO_4$ | 0·20 | — | — |

These figures give the concentration existing in the mixture of sol and electrolyte ; if, *e.g.*, 18 c.c. of the $As_2S_3$ sol is to be coagulated by 2 c.c. of NaCl solution, the latter will have to contain 510 millimoles of NaCl, since by the addition of the sol it is diluted to one-tenth of its original concentration.

A second point to be noted is the difference in the corresponding values, say, for NaCl, between the three negative sols. This may be specific, *i.e.*, a given sol may be much more stable to electrolytes generally than others ; such is the case with the mastic suspension according to different observers. The precipitation concentration, however, also depends on the *concentration of the sol*, and this partly

explains the difference between the $As_2S_3$ and the Pt sol, the former being much more concentrated.

The figures for the $As_2S_3$ sol may be taken as typical for this and for the (dilute) Prussian blue sol, as described, while the figures for the Pt sol will be found approximately correct for the gold sol made by the formaldehyde method. The Prussian blue sol will be found the most convenient for the first experiments.

The next point to be considered is the method of adding the electrolyte solution to the sol. A number of the classical investigations were carried out by titration, *i.e.*, by adding electrolyte solution to the sol until perceptible coagulation took place. This method has the drawbacks that, unless there is a very marked colour change, as with red gold sols, it is by no means easy to notice an exact end-point, that it excludes the time factor, and that the concentration of sol varies with different amounts of coagulating solution. Nevertheless the method gives a rough idea, and may be used for preliminary trials, care being taken to use fairly large volumes of sol and to place the beaker containing it during titration so that small changes in colour or turbidity can be readily noticed.

The procedure to be adopted for exact determinations is as follows: a uniform volume of sol is fixed upon, to which is added a definite fraction of coagulating solution, *the concentration of which is varied.* In this way the sol concentration is kept uniform. The sol and solution are mixed by a uniform procedure, say closing the test tube containing it and reversing it twice or four times; the mixture is allowed to stand for a definite time, say two or three hours, and is then examined.

Eighteen c.c of sol and 2 c.c. of solution will be found convenient, the latter being diluted by the sol to one-tenth of its original concentration. As about

51 millimoles of NaCl, 0·65 of $CaCl_2$, and 0·09 of $AlCl_3$ respectively are the concentrations required *in the mixture* to produce precipitation, the concentrations of the solutions used will have to be ten times greater, viz., 510 millimoles of NaCl, 6·5 of $CaCl_2$, and 0·9 of $AlCl_3$.

Since these concentrations just produce precipitation in a certain sol, it will be desirable to have a considerable margin, and the following three standards for negative sols should be prepared :—

| | | | | |
|---|---|---|---|---|
| NaCl | . 1,000 millimoles | = | 58·5 gm. | in a litre. |
| $CaCl_2$ | . 15 ,, | = | 1·665 gm. | ,, |
| $AlCl_3$ | . 2 ,, | = | 0·267 gm. | ,, |

For very accurate work, or if the materials are of doubtful purity, these solutions should be standardized against suitable standard solutions.

Since one part of these solutions added to nine parts of sol will certainly produce coagulation, more dilute solutions of known strength must be prepared. Do this by mixing in test tubes, say, 8 c.c. of solution with 2 c.c. of water, 6 c.c. of solution with 4 c.c. of water, 4 c.c. of solution with 6 c.c. of water, and 2 c.c. of solution with 8 c.c. of water ; label the tubes 0·8, 0·6, 0·4 and 0·2, these being their respective concentrations referred to the stock solutions.

Now place 18 c.c. of the sol to be examined in each of five test tubes, label them 1, 0·8, 0·6, 0·4 and 0·2, add to each 2 c.c. of the corresponding solution, mix by the standard method decided upon, and allow the tubes to stand for a definite time, say two or three hours. It will then be found, *e.g.*, that the contents of 1, 0·8 and 0·6 have been precipitated, but that those of 0·4 and 0·2 have not changed. The limit concentration accordingly lies between the electrolyte concentrations prevailing in 0·6 and 0·4. The solutions added, if NaCl was used, contained

1,000 × 0·6 and 1,000 × 0·4, *i.e.*, 600 and 400 millimoles respectively; since they were diluted to one-tenth by the sol, the actual concentrations in the mixture are 60 and 40 millimoles. The minimum concentration necessary for precipitation lies between these two; to determine it more accurately, an intermediate concentration of the added solution may now be tried, say 0·5 of the original. For this purpose mix, say, 2 c.c. of stock solution with 2 c.c. of water, and add 2 c.c. of the mixture to 18 c.c. of sol as before. If precipitation just occurs within the standard time, the limit concentration is obviously 1,000 × 0·5/10 = 50 millimoles per litre.

The procedure just described should be carried out with several sols, *e.g.*, Prussian blue, arsenic trisulphide and gold reduced by formaldehyde, *with all three electrolytes*, and the results tabulated. The results should be compared with the numerous data given in the literature and carefully checked if they show very marked deviations from the average. The contents of the sols in disperse phase should also, for comparison, be calculated from the data given for their preparation.

A similar procedure should be adopted with the ferric hydroxide sol, the only representative of the *positively charged* sols. By reference to the table at the beginning of the chapter we find that the limit concentrations are 9·25 millimoles of NaCl and 0·20 of $K_2SO_4$ ($Na_2SO_4$ may be used instead). Using the same ratio as before, 2 c.c. of solution to 18 c.c. of sol, the concentrations of the former will be 92·5 and 2·0 millimoles, and to have the same margin as before we shall require stock solutions of the following concentrations:—

| | | | |
|---|---|---|---|
| NaCl . | 200 millimoles | = 11·7 gm. | in a litre. |
| $Na_2SO_4$ . | 4 ,, | = 0·568 gm. | ,, |

The NaCl solution may, of course, be made up from

that previously used for negative sols by diluting with four volumes of water.

### Literature.

For electrolyte precipitation generally, W. D. Bancroft, Second Report of British Association Committee on Colloid Chemistry, 1918, p. 2. A very complete study of fractional precipitation in Sven Oden, "Der kolloide Schwefel," *N. A. Reg. Soc. Scient. Upsal.*, Ser. IV., Vol. 3, No. 4 (1913). Coagulation velocity: H. H. Paine, *Koll.-Zeitschr.*, XI., 115 (1912); H. Freundlich, and C. Ishizake, Faraday Soc. Gen. Discussion on Colloids and their Viscosity, 1913; H. R. Kruyt and J. van der Speck, *Koll.-Zeitschr.*, XXV., 1 (1919), a very careful study of electrolyte coagulation.

## Chapter XIII.

# MUTUAL PRECIPITATION OF SUSPENSOID SOLS.

Sols in which the disperse phases carry opposite charges precipitate each other when mixed *in definite ratios,* while no precipitation occurs if an excess of either sol is present.

The ferric hydroxide sol described above will, generally speaking, precipitate an *equal volume* of the Prussian blue, the gold sol reduced by formaldehyde, or the mastic suspension. Place 5 c.c. of each of the negative sols into test tubes, add to each 5 c.c. of the (dialysed !) ferric hydroxide sol, mix by a uniform procedure, and allow the tubes to stand. The Prussian blue and the gold sol will generally show coagulation within a few minutes, while the mastic suspension may take 15 to 25 minutes. The coagulum contains *both disperse phases,* so that the liquid in the test tubes is colourless after the former has settled.

If precipitation fails to occur with any of the sols mentioned, or with any other negative sol mixed with an equal volume of ferric hydroxide sol, the correct ratio must be ascertained by experiment. For this purpose place in test tubes 1, 2, 3, etc., up to 9 c.c. of ferric hydroxide sol and add (in the same order) 9, 8, 7, etc., down to 1 c.c. of the negative sol. The contents of each tube must be mixed, by a uniform procedure, immediately after the second sol has been added. After, say, one hour note the ratio in the tube or tubes in which coagulation has occurred.

Examine the electrical condition of two mixtures in which no coagulation has occurred, one having ferric hydroxide, and the other negative sol in excess. For this purpose note the ratios and then make up a sufficient quantity of the mixtures for cataphoresis in the U-tube. The sign of the charge in the mixture will be found to be that of the sol *present in excess*, the charge on the other sol having been reversed.

## CHAPTER XIV.

# PROTECTION.

THE protective effect of emulsoids may be demonstrated in two ways. The emulsoid may be added to one component of a reaction which produces a precipitate and may cause the latter to become much more highly disperse than it would be in a pure aqueous medium. Or the emulsoid may be added to an existing sol, in which case it protects it from electrolytes, *i.e.*, the concentration of the latter necessary to produce coagulation is considerably increased.

To demonstrate the formation of a highly disperse precipitate in the presence of a protective colloid, dissolve 0·5 gm. of crystallized barium chloride in 50 c.c. of water, and 0·25 gm. of ammonium sulphate in 50 c.c. of water. Add 5 c.c. of the first solution to 5 c.c. of the second, and note that the bulk of the precipitate settles in a few minutes.

Warm the ammonium sulphate solution to about 30° C. and add to it 5 c.c. of 15 per cent. gelatin sol, mix thoroughly, and then add the barium chloride solution with continual stirring. The precipitate does not settle out on standing, and the mixture passes through a close filter paper without leaving any residue. Many other precipitates may be obtained as sols in this way by adding to one solution varying amounts of gelatin, albumin or gum arabic, and by choosing suitable concentrations.

The other procedure is to add to a sol, for which the electrolyte concentration required to produce coagulation in a definite time has been previously determined, small amounts of gelatin, albumin or gum arabic sol and to determine what concentration

of electrolyte will now produce a marked change or rapid coagulation. Thus, 9 c.c. of the gold sol made by the formaldehyde method (p. 30) turns blue within a few seconds after the addition of 1 c.c. of N/1 NaCl solution. (Watch this change by pure *transmitted* light, say by looking through the test tube at a uniformly illuminated screen of white paper; reflected light must be excluded, as the strong reddish-brown surface colour of the sol is almost the same for the original red as for the blue sol and makes observation of the change difficult.) Now add to 9 c.c. of the same sol 1 c.c. of a 0·1 per cent. gelatin sol (0·1 gm. in 100 c.c.), mix well, add 1 c.c. of the N/1 NaCl solution, and note that *no change of colour* occurs, even on standing. Add more NaCl solution, 1 c.c. at a time, and note that even 4 or 5 c.c. produces no change whatever.

*Gold Numbers.*—The gold number of an emulsoid is defined by R. Zsigmondy as the number of milligrammes of the emulsoid just sufficient to prevent a colour change in 10 c.c. of a standard red gold sol on addition of 1 c.c. of a standard solution of NaCl (density 1·07, *i.e.*, concentration about N/1). As these figures are arbitrary, it is better to state the *percentage concentration of emulsoid in the gold sol* which just prevents the colour change when 1 c.c. of N/1 NaCl solution is added to about 10 c.c. of sol. The following figures have been calculated from Zsigmondy's gold numbers :—

| Emulsoid. | Minimum concentration in per cent. which prevents colour change. | |
|---|---|---|
| Gelatin . . . . | 0·00005 | to 0·0001 |
| Egg albumin (dry, commercial) . . . . | 0·001 | to 0·002 |
| Gum arabic . . . | 0·0015 | to 0·0025 |
| Dextrin . . . . | 0·10 | to 0·20 |
| Potato starch . . . | 0·25 | — |

These are exiguous concentrations, especially for the most active protective agents; if 1 c.c. of emulsoid sol is to be added to 10 c.c. of gold sol, the concentrations of the former will have to be 11 times those given in the table, *e.g.*, 0·00055 to 0·0011 per cent., or 0·0055 to 0·011 gm. per litre, for gelatin. It is advisable to make up sols of still greater concentration, say 50 times those given in the table, preferably by suitable dilution of any concentrated sols available in the laboratory.

Then proceed as follows: Place 10 c.c. of gold sol, which should be a pure red without any purple tinge, into each of a number of test tubes, add 0·1, 0·2, 0·4 up to 1 c.c. of emulsoid sol and mix. Then add to each test tube 1 c.c. of N/1 NaCl and note the concentrations in the tube which just retains the red colour and the next one, which shows the change to blue. If, for instance, the tube with 0·2 c.c. of emulsoid sol remains unaltered and the one with 0·1 has turned; the emulsoid concentrations are respectively:—

$2/102 = 0{\cdot}0196 \times$ original emulsoid concentration.
$1/101 = 0{\cdot}0099 \times$ „ „ „ .

The gold number in percentage lies between these values and may be determined more exactly by using intermediate volumes or by reducing the concentration of the emulsoid sol used and repeating the series.

The gold numbers are a delicate means of differentiating between proteins which cannot readily be distinguished by other tests. The method has, therefore, acquired some importance in medical and biochemical work, which is, however, beyond the scope of this book.

*Behaviour of different Sols.*—The protective effect of a given emulsoid sol is not necessarily the same on other sols as on gold sols; apart from the question

of concentration there appear to be specific differences, although, generally speaking, the various emulsoids stand in the same order for most sols as they do for gold sols. To show this, determine approximtely the volume of N/1 NaCl solution necessary to coagulate 10 c.c. of the (dilute) Prussian blue sol. Add 1 c.c. of the 0·1 per cent. gelatin sol previously used with gold sol to 9 c.c. of Prussian blue sol, then add the volume of sodium chloride solution found sufficient to coagulate the unprotected sol. Generally this will be sufficient to precipitate the protected sol after a somewhat longer time, notwithstanding the presence of an amount of gelatin which, in the previous experiment, completely protected the gold sol.

### Literature.

For protective effect and gold numbers, see Zsigmondy-Spear, "Colloidal Chemistry" (Chapman and Hall, 1917), pp. 106—111; "Investigations on a Number of Protective Agents, chiefly of Vegetable Origin," by A. Gutbier and collaborators, *Koll.-Zeitschr.*, XVIII., 1, 57, 141, 201; XIX., 22, 90, 177, 230 (1916); XX., 123, 186 (1917).

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## CHAPTER XV.

# VISCOSITY MEASUREMENTS.

THE only suitable instrument for accurate determinations is a properly designed capillary viscometer. The various rough methods employed occasionally, such as determining the time required for a given volume to flow from a pipette, or the time taken by a small sphere to fall through a given height, are useless, as in all these arrangements the time measured is very far from being simply proportional to the viscosity.

Two types of capillary viscometers may be used: the simple Ostwald type (Fig. 16), in which the flow is caused by the difference of head in the two limbs of the instrument, and the Ubbelohde type (Fig. 17), in which the flow is caused by a constant air pressure applied to one limb. The use of the latter and the manostatic apparatus for providing constant air pressure will be described later.

The Ostwald viscometer consists of a wide tube, generally provided with a bulb at the lower end, which is joined by a bend to a straight capillary tube. The latter leads into a bulb capable of holding 2 to 3 c.c. of liquid, and provided with an inlet tube, a constriction being provided where this tube joins the bulb. Marks are placed, one in the centre of the constriction and one below the bulb at the beginning of the straight capillary. The instrument is generally used only for determining *relative* viscosities, *e.g.*, the viscosity of a sol referred to the viscosity of the pure dispersion medium as unity. In this case all the factors in Poiseuille's formula which depend

on the measurements of the instrument remain the same, and the pressures in the case of two liquids

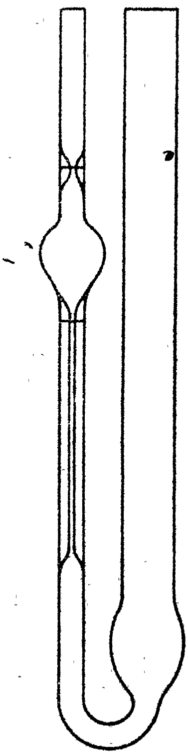

FIG. 16.

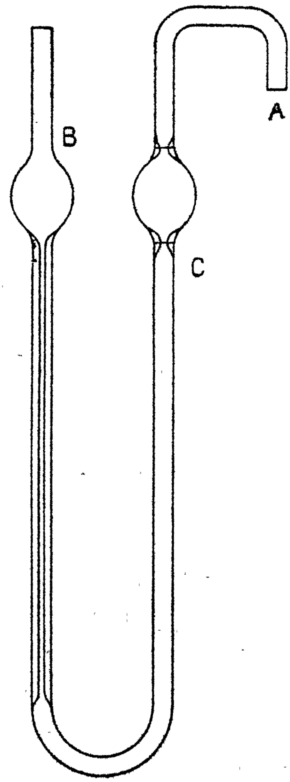


FIG. 17.

having the densities $\rho_0$ and $\rho_1$ are simply proportional to these densities, provided the same volume is used, so that the effective height of the liquid is the same in both cases. If the times taken by the

level of the liquid in sinking from the upper to the lower mark are respectively $t_0$ and $t_1$, the viscosities $\eta_0$ and $\eta_1$ are in the following ratio :—

$$\eta_0 : \eta_1 = t_0\rho_0 : t_1\rho_1$$

and the relative viscosity $\eta_1$

$$\eta_1 = \eta_0 \frac{t_1\rho_1}{t_0\,\rho_0}$$

It is accordingly necessary to determine the density of the liquids under examination, and it need hardly be added that this must be done *at the temperature or temperatures at which the viscosities are to be measured.*

To use the instrument it is first mounted vertically, by sighting it with a plumb-line in two directions at right angles to each other. A definite volume of liquid is then run into the wide tube from a pipette reserved for this purpose. A convenient length of rubber tube is fitted to the top of the bulb and the liquid drawn up through the capillary until it has filled the upper bulb and risen well above the upper mark, when the tube is closed by pinching with the left hand. (Sufficient liquid must be delivered by the pipette to leave some liquid in the lower bulb when this has been done.) A stop-watch is held in the right hand, the rubber tube released and the watch started when the level of the liquid passes through the upper mark, and stopped when it passes through the lower mark. *The eye should be kept on the viscometer and not on the watch.*

As viscometers are not readily obtainable, they will generally have to be blown specially, when the following points are to be noted. For sols with water as dispersion medium and, therefore, requiring the time of outflow of water to be determined, capillaries about 0·5 to 0·6 mm. bore will be suitable. The length of the capillary should be 80 to 100 times the diameter of the bore, say 5 to

6 cm. at least. A bulb holding 2 to 2·5 c.c. on the end of the capillary is convenient, and the diameter of the inlet tube, as well as that of the bend connecting the capillary with the wide tube, should not be less than 3 mm., preferably 4 mm. The change in diameter from the bulb into the capillary, and from the latter into the bend, should be smooth and gradual. The time of flow should not be less than 60 seconds for water at 20° C.

Viscometers conforming to this description will be suitable for measuring viscosities up to 20 or 25 times that of water, *i.e.*, for fairly concentrated emulsoid sols. Sols having organic dispersion media, such as rubber-benzene sols, or sols of nitrocellulose in various media, however, often have viscosities of much larger order even in moderate concentrations, and it is then not feasible to carry out the whole series of measurements with the instrument used for the dispersion medium. A range of viscometers of increasing bore, and proportionately increasing length of capillary, must then be provided. The readings made by two instruments, say one used for the dispersion medium and for relative viscosities up to 20, and the next instrument, are then connected with each other in the following manner. The time of efflux for the most concentrated sol, for which the first instrument can be used, is determined and found to be $n_1$. The time of efflux for the *same* sol is then determined in the second instrument and found to be a smaller value, $n_2$. To reduce readings on the second instrument to those on the first, and eventually to relative viscosities, they must, therefore, be multiplied with $n_1/n_2$. Instead of the sol itself any sufficiently viscous liquid may be used to determine this ratio; glycerine or mixtures of glycerine with (little) water may be employed.

Viscometers must be thoroughly cleaned immediately before use with hot dichromate-sulphuric

acid mixture, followed by distilled water and then by alcohol and ether, which is dried off by blowing air *filtered through glass wool* through the instrument. The latter precaution is necessary, as even small particles of dust may vitiate results seriously, in view of the small bore of the capillary. For the same reason the liquids to be investigated should be filtered, or, where this is not possible, at least strained through a glass wool plug.

Since viscosity decreases to the extent of 3 to 5 per cent. per degree of temperature in pure liquids, and at a much higher rate in emulsoid sols, it is absolutely essential that measurements should be carried out in a thermostat in which it is possible to keep temperatures constant within 0·1° C. Where a proper apparatus is not available a beaker holding at least two litres may be used. The viscometer, a thermometer divided into tenths of a degree, and the toluene regulator are supported in the water from a suitable stand, and some form of stirrer must be arranged. The beaker stands on asbestos-coated wire gauze on a tripod, and is heated by a small—pin-hole or "micro"—gas burner, which must, however, be sufficient to keep the water at the required temperature, *i.e.*, to make up the heat lost by convection and radiation. The water may be heated up to within a degree of the required temperature by a Bunsen burner, and the small burner substituted for it then. The regulator is then adjusted so as to cut off about the required temperature; since it is somewhat troublesome to do this with complete accuracy, it is better to take readings within 0·2 or 0·3° of round numbers rather than to spend much time in trying to set the regulator exactly to the latter. Thus, if measurements at, say, five degrees' intervals are wanted, it will be quite permissible to work at 20·3°, 25·1°, 30·0°, etc., provided the results are plotted accurately.

The temperature regulation may fail in two ways: either the temperature may fall, although the regulator is fully open—in that case the gas pressure or the size of the burner is insufficient; or the gas regulator may fail to cut off, although the temperature keeps rising—this trouble is generally due to "creeping" of the toluene, which passes between the mercury and the glass, instead of raising the mercury. This can be corrected by renewing the toluene and thoroughly cleaning the mercury. The trouble is much less frequent if a concentrated solution of calcium chloride in water is substituted for the toluene.

The determination of the density—unless required for some further reason—is tedious and can be avoided by the use of the viscometer illustrated in Fig. 17, in which the pressure causing the flow is produced by compressed air instead of by the head of liquid itself. The instrument has two bulbs of equal size; one limb of the U connecting the bulbs is a capillary of suitable bore, while the other is a wider tube. The liquid is drawn into the viscometer through A, and a definite volume must be used, so that, when the level is at B in the bulb on the capillary side, it stands at C in the opposite limb. When pressure is applied on the side containing the capillary, the liquid rises into the opposite bulb, and, finally, the difference of levels is equal and opposite to that which prevailed at the beginning, so that the effect of the liquid head, and, therefore, of the density, is eliminated.

The pressure is generated by the simple manostat shown in Fig. 18. A Mariotte's bottle A discharges water through a rubber tube and a piece of glass tube turned upwards at a right angle into a second bottle B of the same size. A Tee-piece passing through the stopper in the top of the bottle is connected at C to a water pressure gauge and at D to the viscometer,

which is fitted with a three-way stop-cock. The active column of water is that between the bottom of the air tube of the Mariotte bottle and the top of

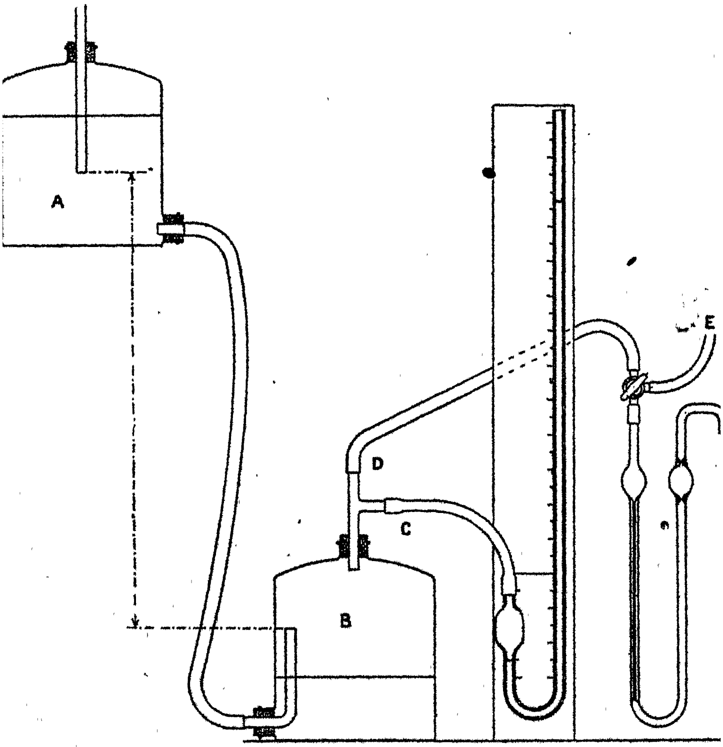


FIG. 18.

the bent tube discharging the water, and the gauge must, of course, have a limb of somewhat greater length than this height.

Before using the apparatus, water is allowed to flow into the lower bottle until the column in the

gauge becomes stationary. While this is being done the three-way cock is turned so as to shut off the compressed air tube from the viscometer and to leave the latter open to the atmosphere. The viscometer is now filled with the required volume of liquid, which is drawn up into the left-hand limb above the bulb by suction applied at E. The cock is then turned so as to shut off the viscometer from the atmosphere and leave the compressed air supply also shut off. The stop-watch is now got ready, the compressed air admitted to the viscometer, and the watch is released as the liquid passes through the lower mark and arrested when it passes through the upper mark. All measurements in one series are, of course, carried out with the same air pressure, *i.e.*, without altering the column of the manostat. *The time between marks is then directly proportional to the viscosity.*

It is hardly necessary to add that this type of instrument, like the Ostwald viscometer, must be kept in a thermostat. In both cases it is essential to make sure that the liquid under examination has reached the temperature indicated by the thermometer in the water bath; this is the case if two readings taken at an interval of, say, five minutes do not differ by more than 1 per cent. at the outside. Generally speaking, three determinations on the same specimen should always be made and the arithmetical mean taken as the final result, provided the three readings do not differ by more than 1 per cent. If the readings *decrease*, the temperature may still be rising, as already pointed out; if, however, the decrease becomes more marked on repetition, the viscosity of the sol is being reduced through its being forced through the capillary. This phenomenon is quite common with many emulsoid sols and very marked, *e.g.*, with starch sols.

If the readings *increase* on repetition (provided, of

course, that the thermostat is working properly), the capillary is becoming blocked, either by accidental contamination with dust, etc., or by adsorption or coagulation on its wall. In that case the instrument must be removed and thoroughly cleaned in the manner already described.

In general series of viscosity measurements will be carried out to determine, *e.g.*, the change in viscosity with concentration, or—concentration being constant—with temperature. In both cases the results should be plotted on sectional paper, to a fairly large scale, with the variable concentration (or temperature) as abscissa and the viscosity as ordinate. The latter is, of course, proportional to the product: time × density, if the Ostwald viscometer is used, and to the time only with the Ubbelohde viscometer. The points found should, in general, lie very nearly on a smooth curve; cusps or inflexions occur only where coagulation or the like takes place. Points which fall outside a smooth hyperbolic or logarithmic curve to a marked extent are, therefore, suspect unless such disturbing phenomena are at all probable, and the particular reading should be carefully repeated.

To practise the use of the apparatus the beginner will find gum arabic sol convenient. Five concentrations, say 5, 10, 15, 20 and 30 per cent., should be prepared, filtered through glass wool and the viscosities determined at some convenient temperature, say 2° or 3° C. above that of the room. The sols should be prepared when required. For viscosity-temperature measurements a sol made from 30 gm. of gelatin in 100 c.c. of water is convenient, made and filtered in the usual way. Measurements should be begun with the thermostat at, say, 45° or 50°; the temperature is then allowed to fall about 5°, the regulator readjusted and a reading taken, and this procedure is continued until the setting temperature

of the sol is reached. The results may be plotted directly, *i.e.*, as the products time × density; a clearer insight is, however, gained by plotting *relative viscosities with water at the same temperature taken as unity.* The viscosity of water at different temperatures may be found in tables, or be determined in a second viscometer placed in the thermostat; the densities of water at different temperatures are given in most works of reference. The quantities to be plotted will then be, if the times of efflux and the densities of the sol at the temperatures 1, 2, etc., are $t_1$ and $\rho_1$, $t_2$ and $\rho_2$, etc., and the corresponding figures for water $t'_1$ and $\rho'_1$, $t'_2$ and $\rho'_2$.

$$\eta_1/\eta'_1 = t_1\ \rho_1/t'_1\ \rho'_1;\ \eta_2/\eta'_2 = t_2\ \rho_2/t'_2\ \rho'_2, \text{ etc.}$$

A curve plotted with these relative viscosities as ordinates against temperatures as abscissæ shows that the temperature coefficient of the sol is much greater than that of water, *i.e.*, the percentage decrease with rising temperature is much greater than that of pure water.

### LITERATURE.

See, generally, Faraday Soc. Gen. Discussion on Colloids and their Viscosity, 1913; copious references to experimental work are given in this, especially in Wo. Ostwald's contribution.

## CHAPTER XVI.

# ADSORPTION (QUALITATIVE EXPERIMENTS).

THE removal of solutes from solution by solids having a large surface can be shown in a great variety of ways. Solutions of dyes, *e.g.*, crystal violet, methyl violet, methyl green, etc., containing 2 to 3 mg. in 100 c.c., may be shaken with 2 to 3 gm. of charcoal, fuller's earth or china clay, and will generally be found colourless after the adsorbent has settled. The adsorption of lead salts is another striking example. Add to 100 c.c. of water 2 or 3 drops of concentrated solution of lead nitrate, take 5 c.c. of the mixture and note the reaction with ammonium sulphide. Then shake the bulk with 4 to 5 gm. of charcoal, filter and test the filtrate with ammonium sulphide; with moderately good brands of charcoal no reaction, or at most a very faint brown tinge, will be visible.

*Influence of Solvent on Adsorption.*—Dissolve 2 to 3 mg. of methyl violet in 100 c.c. of water, shake with 2 gm. of charcoal and allow the latter to settle; the supernatant liquid is generally colourless. Pour it off as far as possible, and pour on the charcoal 80 to 90 c.c. of alcohol or acetone. This immediately assumes a violet colour, showing that the equilibrium concentration in the organic solvent is higher than in water, *i.e.*, the amount adsorbed from it is smaller.

*Adsorption due to Neutralization of Electric Charges.*—A glass tube, about 25 mm. diameter and about

60 cm. long, is held vertically in a suitable clamp. The lower end is closed by a rubber stopper, through which passes a short piece of glass tube about 4 mm. diameter, the upper end of which is flush with the surface of the stopper, while the lower projects 1 or 2 cm. Place a loose plug of glass wool on the stopper, and then fill the tube to half its height with silver sand, which has been washed with nitric acid followed by water, and has then been dried and ignited. Then fill the tube with ferric hydroxide sol and collect the liquid which escapes from the outlet tube in a beaker. This is quite colourless, the ferric hydroxide, which is positive, having been discharged and retained by the negatively charged quartz grains. If Night blue, a dye which is also positively charged in aqueous dispersion, can be obtained, the sol may be used instead of ferric hydroxide; 2 to 4 mg. in 100 c.c. is a suitable concentration.

Similar results may be obtained by allowing strips of filter paper (which also takes a negative charge in water) to dip into sols. If the latter are positive, only water rises, the disperse phase being coagulated at the level of the liquid; if the sol is negative, no separation occurs and the colour, *e.g.*, of Prussian blue, rises in the strip.

*Selective Adsorption.*—An example can be demonstrated as follows: Dissolve 5 gm. of gelatin in 50 c.c. of water in the usual manner, and pour the sol into shallow moulds, so as to obtain strips or discs 3 to 4 mm. thick. Remove these from the moulds after 12 hours, and place them in a flat porcelain (developing) dish containing about 150 c.c. of a 2 per cent. solution of *commercial* aluminium sulphate. Place 10 c.c. of the solution in a test tube, add a few drops of ammonium thiocyanate, note that the solution shows a marked iron reaction, and set the sample aside. After lying in the solution for three or four days the gelatin shows a marked

reddish-brown tinge due to ferric iron; if a 10 c.c. sample of the solution, in which the gelatin is lying, is again tested with thiocyanate and compared with the original sample, the iron content will be found to be much reduced.

## CHAPTER XVII.

# CAPILLARY ANALYSIS.

THIS is a method of separating and detecting various constituents of a mixture by means of the difference in their rates of diffusion and adsorption. The usual procedure is to allow the solution containing the several solutes to rise in strips of white filter paper; the various constituents rise to different heights, and may be detected by their colour, or by suitable reagents applied to different portions of the strip.

The strips should be cut from a white, neutral filter paper (Whatman No. 2 is suitable) about 1 cm. wide and 25 to 30 cm. long; the edge of the sheet must not be used. They are then suspended vertically, with their lower ends dipping about 2 cm. into the liquid to be examined. Evaporation must be prevented; for single experiments the simplest way is to place the liquid in the bottom of a tall cylinder and suspend the strip from the stopper, care being taken that it hangs vertically and does not touch the wall. The liquid is allowed to rise until it becomes stationary or for a fixed time, say 6 to 9 hours, and the strip is then examined and tested.

The following is a convenient example for showing the delicacy of the method. Slice about 100 gm. of boiled beetroot, pulp the slices with 50 c.c. of 5 per cent. acetic acid, place the pulp into a muslin bag and express about 50 c.c. of liquid, which need not be filtered. Take 5 c.c. of the liquid and add to

it gradually in a test tube N/25 caustic soda solution; the colour changes to purple, brown and, finally, to a dirty greenish yellow. Now add to the 45 c.c. of liquid three to five (burette) drops of the methyl orange used as indicator. This turns red, the colour being entirely masked by the deep red of the solution; the colour change with alkali is similarly masked, as the beetroot pigment also turns yellow. Place the liquid to which methyl orange has been added into a tall cylinder and suspend a strip of filter paper as previously described. The strip is gradually stained a fairly uniform purplish red. When this has reached a height of about 16 or 18 cm. remove the strip, let it drain for a few minutes and then dip it into N/25 solution of NaOH, removing it immediately. The clear yellow of the methyl orange turned by alkali is very plainly visible at the top, over a width of 2 or 3 cm., while the rest of the strip still remains purple or red. If the strip is immediately rinsed, dried and kept in the dark, the result may be preserved permanently; failing this, the lower portion gradually gets discoloured.

Another mixture suitable for demonstrating the method is made by extracting 5 gm. of turmeric with 30 to 40 c.c. of hot water, filtering and adding to the filtrate about 1 c.c. of concentrated picric acid. The mixture stains the filter paper a fairly uniform yellow; when dipped in dilute caustic soda, the lower portion turns brown, while the upper, which contains the acid only, remains yellow with sodium picrate.

The method is capable of very wide application. It has been developed, and its possibilities demonstrated, chiefly by F. Goppelsroeder, whose work unfortunately has appeared chiefly in publications not generally accessible. A number of papers covering a very wide field were published in the *Kolloid-Zeitschrift*, and are given below.

## Literature.

F. Goppelsroeder, *Koll.-Zeitschr.*, V., 52 (salt solutions), 109 (foods and beverages), 159 (mineral waters), 200 (vegetable pigments), 305 (urine) (1909); VI., 42 (urine continued), 111 (vital staining of plants), 174 (vital staining of animals), 213 (vital staining of animals continued), 268 (constitution of dyes and vital staining) (1910).

## CHAPTER XVIII.

## DETERMINATION OF AN ADSORPTION ISOTHERM.

A COMPARATIVELY simple and satisfactory instance is the adsorption of oxalic acid by charcoal, the acid concentration being determined by titration with potassium permanganate.

Dissolve 10·5 gm. of crystallized oxalic acid ($C_2H_2O_4 . 2H_2O$) to make 250 c.c. of solution. Then place into five conical beakers or Erlenmeyer flasks of 100 to 150 c.c. capacity the following: 50 c.c. of the original acid solution; 40 c.c. of solution and 10 c.c. of water; 30 c.c. of solution and 20 c.c. of water; 20 c.c. of solution and 30 c.c. of water, and 10 c.c. of solution and 40 c.c. of water. Label the beakers in the same order, 5, 4, 3, 2 and 1 respectively, these being the ratios of their original concentrations.

Place in each beaker 1 gm. of finely powdered charcoal and shake well at intervals, and finally allow the powder to settle overnight.

We have now to consider the choice of a suitable strength for the permanganate solution. The solution (1) has a concentration *before adsorption* one-fifth of that of the initial solution, and this will presumably be considerably reduced. The final concentration *after adsorption* should, however, still be capable of accurate determination, and we shall, therefore, do well to choose a permanganate solution so dilute that, say, 25 c.c. of it will be required to oxidize 5 c.c. of the starting solution.

The concentration* of the latter ($C_2H_2O_4 . 2H_2O = 126$) is M/3, and we shall, therefore, require $2KMnO_4/15$ for complete oxidation of one litre of solution, *i.e.*, 21·086 gm. Since, however, we have settled that 5 c.c. of permanganate solution should equal 1 c.c. of the original acid solution, we shall require one-fifth of that concentration, *i.e.*, 4·217 gm. per litre. It will not be necessary to make up a litre, but 500 c.c. (containing 2·108 gm.) should be made up *with freshly distilled water*. This leaves an ample reserve for repeating any of the experiments which, when the isotherm comes to be plotted, appear doubtful; a reserve of oxalic acid is also provided for by the figures given above.

The first operation is, of course, to determine the actual ratio of permanganate solution to oxalic acid. Titrate 5 c.c. of the stock solution with the permanganate solution in the usual way, hot in presence of sulphuric acid. Suppose the figure found is 26·1 c.c. (instead of 25). Then 5 c.c. of the solutions (4), (3), (2) and (1) will respectively require 20·88, 15·66, 10·44 and 5·22 c.c. of permanganate.

Five c.c. of each of the solutions is now pipetted off, without disturbing the sediment of charcoal, and titrated. Begin with (5), remember the original titre, 26·1 c.c., *bear in mind that the concentration will be perceptibly reduced and, therefore, go slowly.* If, as will quite possibly happen in one case or another, the end point is overrun, the determination must, of course, be repeated. Assuming that the sample (5) after adsorption requires 17·2 c.c. only, acid equivalent to $26·1 - 17·2 = 8·9$ c.c. has disappeared from solution by adsorption. In proceeding to the other samples, remember that the amounts which have been adsorbed will be *smaller absolutely but greater relatively*. As charcoal varies very considerably,

* In this chapter "M" is used to denote a concentration of one mole (gramme-molecule) per litre.

no definite figures can be given for guidance. The results of a series of determinations, made exactly as described, are, however, given below.

Five c.c. of original acid solution requires 26·5 c.c. of $KMnO_4$.

| | (5) | (4) | (3) | (2) | (1) |
|---|---|---|---|---|---|
| 5 c.c. of solution requires c.c. of $KMnO_4$ before adsorption . . . | 26·5 | 21·2 | 15·9 | 10·6 | 5·3 |
| 5 c.c. of solution requires c.c. of $KMnO_4$ after adsorption . . . | 17·5 | 12·5 | 7·8 | 3·8 | 0·8 |
| Difference, *i.e.*, amount adsorbed, in c.c. of $KMnO_4$. | 9·0 | 8·7 | 8·1 | 6·8 | 4·5 |

Since all our units are arbitrary, we can write the usual adsorption formula in the simple form:

$$y = a\,C^{\frac{1}{n}}$$

where $y$ is the amount adsorbed and C the equilibrium concentration. The latter, expressed in cubic centimetres of permanganate solution, is given by the figures in the second row, while the figures in the third row give the $y$ in the same units. We can, therefore, plot the C as abscissæ and the $y$ as ordinates on sectional paper to a convenient scale, say 1 c.c. = 1 cm. The points so obtained should lie on a smooth curve of the familiar parabolic type (Fig. 19). If any points fail to do so, the corresponding determination should be immediately and carefully repeated.

Although the curve obtained may be smooth and have the general appearance of the adsorption isotherm, it is not possible to say definitely that it conforms to the equation without a further test. If we take the logarithms on both sides, we find:

$$\log y = 1/n \log C + \log a,$$

which, taking log $y$ and log C as co-ordinates, is the equation of a *straight line*. To test the nature of the curve we must, therefore, plot the logarithms of

*y* and C as ordinates and abscissæ respectively; this can be done by plotting the *actual figures on logarithmically ruled paper*, or, if this is not available, by taking the logarithms and plotting them to a convenient scale, say 0·1 = 1 cm., on ordinary millimetre paper. The logarithms in that case should be taken to three

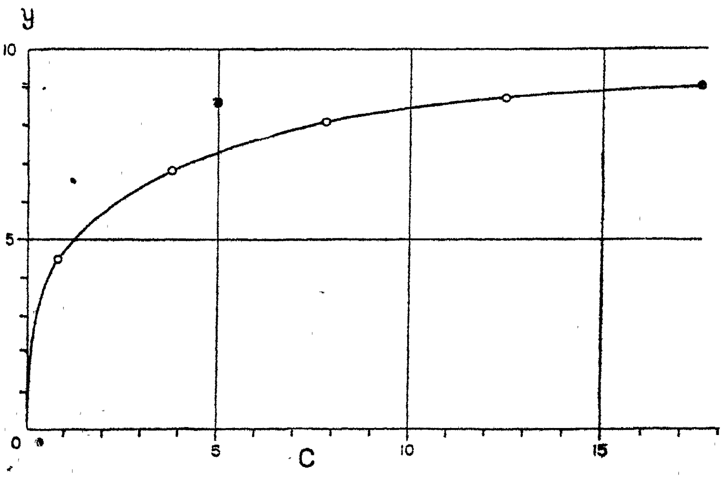


FIG. 19.

figures, with the last figure corrected. We thus obtain the following values for the results found above:

| | (5) | (4) | (3) | (2) | (1) |
|---|---|---|---|---|---|
| log C . | 1·243 | 1·097 | 0·892 | 0·580 | 0·903−1 = −0·097 |
| log *y* . | 0·954 | 0·940 | 0·908 | 0·833 | 0·653 |

These values have been plotted, log C as abscissæ and log *y* as ordinates, in Fig. 20, and lie very nearly on a straight line. The deviation is not greater than appears in most of the log *y*—log C curves to be found in the literature. Whether it is due to experimental error or actually denotes a departure from

the ideal type of isotherm can only be determined by further test, *i.e.*, by repetition of the titrations of (2) and (1), and by determining two further points, say one intermediate and one below (1). Suitable mixtures would be 15 c.c. of the original acid solution with 35 c.c. of water, and 5 c.c. of the original acid solution with 45 c.c. of water. As the acid in the latter will be almost completely removed, it may be

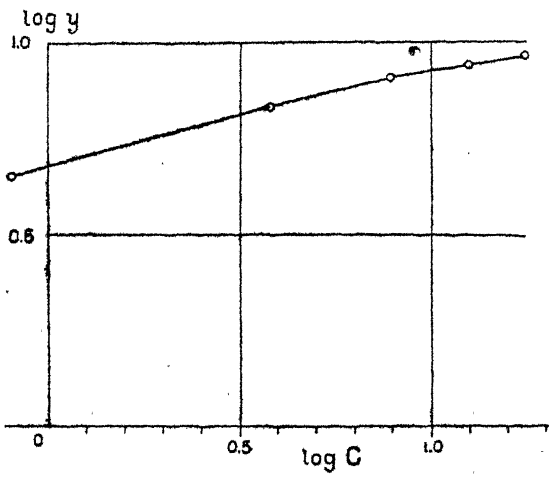


FIG. 20.

advisable to carry out the titration with 10 or 15 (instead of 5) c.c., the result being reduced to 5 c.c. by calculation. In view of the smoothness of the $y$—C curve, the deviation from the straight line, and, therefore, from the ideal isotherm, is probably real.

The log $y$—log C diagram may be used for determining the value of $n$ in the equation of the isotherm, since $n = \log C/(\log y - \log a)$ is the cotangent of the angle made by the straight line with the C-axis.

Calculated from the straight line joining the points (2), (3), (4) and (5), this in the present case would be 5·5, so that $1/n = 0{\cdot}18$, which, although low, comes well within the range of observed values of $1/n$. Log $a$ is, of course, the value assumed by log $y$ when log C = 0, *i.e.*, the length cut off by the straight line on the $y$-axis; in the diagram given log $a$ is about 0·68.

Although the adsorption isotherm and the log $y$—log C curve may be plotted with arbitrary units as co-ordinates, for any given solute, *comparison with another substance is only possible if the results are expressed as molar concentrations.* This, however, is simply a matter of calculation. Our original acid solution contained M/3 of oxalic acid. Solution (3), *e.g.*, therefore contained $M/3 \times 3/5 = M/5$. After adsorption 5 c.c. of (3) required 7·8 c.c. of permanganate solution. Since 5 c.c. of the original, M/3 solution, required 26·5 c.c., we obtain the molar concentration of (3) *after adsorption*, $x$, from the proportion:

$$M/3 : x = 26{\cdot}5 : 7{\cdot}8$$
$$\therefore x = M/10{\cdot}2.$$

We therefore know that 1 gm. of the charcoal used, placed in 50 c.c. of M/5 solution of oxalic acid, leaves an equilibrium concentration of M/10·2. This enables us to compare oxalic acid with, say, another organic acid, *using, of course, the same quantities and concentrations, i.e.*, 1 gm. of the same charcoal and 50 c.c. of M/5 solution of the other acid.

The example discussed has been chosen as being particularly simple for two reasons: the solute can be used in fairly high concentrations, and the method of titration is a very accurate one. Similar conditions, if not quite so favourable, obtain with other organic acids, the concentrations being determined by ordinary acidimetric methods. Adsorption from mixtures can be studied when a specific method is

available for titrating one constituent ; thus adsorption from mixtures of oxalic and some other acid can be investigated by determining the *whole acid content* acidimetrically, and the concentration of oxalic acid, in a parallel sample, by permanganate.

In most cases the difficulties are, however, considerably greater, and resolve themselves chiefly into finding analytical methods of sufficient delicacy to determine small differences of small concentrations. Thus with many dyes the whole range of concentrations investigated may be much below 0·1 per cent., while no specific method of titration is available. Determinations of this kind have been made by colorimetric methods. If the solute is optically active, concentrations may be determined by the polariscope, provided, of course, that *the specific rotation does not vary with the concentration*, a point which must be ascertained by experiment with a few solutions of *known strength and approximately covering the range to be investigated.*

In determining the adsorption curve the assumption is made that an equilibrium has been reached. Although this is, roughly speaking, true in many cases, numerous instances are known in which small amounts of solute continue to disappear from the solution. The effect of this continued sorption may show itself even in the time which necessarily elapses between the first and the last titration, *i.e.*, the values found for the samples last examined are somewhat higher relatively than those for the first, a discrepancy which would show itself particularly in the log $y$—log C curve. If there is reason to suspect this phenomenon, the liquid should be left on the adsorbent and determinations repeated at intervals of some days. The causes may be various, *e.g.*, the adsorption on the coarse external surface of the adsorbent is followed by slow diffusion into the pores with further adsorption on the surface of the latter :

or chemical action may follow adsorption, a possibility which, although apparently remote, has been proved real in some instances; or, finally, the physical condition of the adsorbent, and, therefore, its specific surface, may change.

For theoretical work finely powdered charcoal, especially blood charcoal, is the most satisfactory adsorbent; fuller's earth, china clay, etc., give discrepant results more frequently. Whatever adsorbent is selected, an amply sufficient quantity to carry out and repeat experiments should be obtained before starting.

### LITERATURE.

For adsorption by solids from solution, see H. Freundlich, "Kapillarchemie," Leipzig, 1909, pp. 145—173. Recent papers: G. v. Georgievics, *Monatsh. f. Chem.*, 34, 733 (1913), ads. of acids by wool; T. Oryng, *Koll.-Zeitschr.*, XIV., 14 (1913), negative ads.; K. Estrup, *Koll.-Zeitschr.*, XIV., 8 (1914), ads. of electrolytes; Sorption of iodine by carbon, J. W. McBain, *Trans. Faraday Soc.*, XIV., Part 3 (1919); C. Koch, *Koll.-Zeitschr.*, XXII., 1 (1918), adsorption of sodium aurichloride on charcoal; a good example of adsorption in very low concentrations.

## Chapter XIX.

# THE LIESEGANG PHENOMENON.

R. E. Liesegang's original prescription is as follows: 4 gm. of gelatin is dispersed in 100 c.c. of water in the usual way, and 2 c.c. of a concentrated solution of potassium dichromate added to the sol. The mixture is poured on clean glass plates to form a thin layer, about 0·45 c.c. per square inch of surface being allowed. The plate is supported on a horizontal surface and the sol allowed to set; 10 to 15 minutes will be required, according to the temperature of the room. A large drop of 20 to 30 per cent. solution of silver nitrate is placed in the centre of the plate, preferably by allowing five successive drops of about 0·1 c.c. each to fall on the same spot from a small pipette drawn into a sufficiently fine point. If this operation is properly carried out, the drop should have a clean circular outline. The plate is kept in the dark for 24 to 48 hours (as light acts on gelatin containing dichromate), but may be examined from time to time in diffuse light. At the end of this period any traces of the original drop still remaining may be removed with a pointed strip of filter paper, and the gel is then allowed to dry. The silver chromate resulting from the reaction will be found to form numerous concentric circles round the edge of the original drop, separated by clear zones free from precipitate and increasing in width from the centre outwards.

The following details should be noted. The plates must be quite clean and, in particular, free from traces of grease. To cover them with gelatin right

up to the edge is an operation requiring considerable practice, and the beginner may be satisfied with a uniform layer extending to within $\frac{1}{2}''$ of it. The plate should be slightly warmed and held in the left hand an inch or two above the horizontal surface on which the plate is eventually allowed to cool, while the whole amount of sol is poured slowly on the centre and uniformly spread by slightly inclining the plate as may be necessary. After cooling and *before* putting on the silver nitrate the plate should be placed where it can be left undisturbed for the rest of the time, as the drop easily spreads if the plate is moved.

To produce really good rings the gelatin must contain a small amount of acid and of gelatose (a product of hydrolysis which does not gelatinize on cooling). Inferior commercial brands of gelatin happen to contain these two constituents in the right proportion, while particularly "hard" gelatins may require a slight addition of either or both. Liesegang recommends citric acid as particularly suitable, and the addition of 5 to 10 drops of a 5 per cent. solution to 100 c.c. of sol may be tried if a particular brand of gelatin does not give good rings. Similar quantities of gelatose may also produce marked improvement; it may be prepared by prolonged boiling of a 10 per cent. gelatin sol (evaporated water being replaced), which is continued until a sample placed on a cold glass surface no longer sets to a jelly. Suitable proportions of either or both constituents increase the width of the chromate rings until, with excessive amounts, the whole precipitate forms a continuous band. Instead of adding gelatose it may also be produced in the sol itself by keeping it at high temperature for several hours; the dichromate must, of course, not be added until this operation is complete, as it would undergo partial reduction.

The experiment may also be carried out in a somewhat different manner. A test tube is filled to about

two-thirds of its height with the dichromate-gelatin sol, which is allowed to set, and a few cubic centimetres of the silver nitrate solution is then poured on top of the gel. Other reactions, however, give better results with this procedure, among which the following are particularly suitable for study :—

*Tricalcium Phosphate in Gelatin.*—Dissolve 3 gm. of crystallized tribasic sodium phosphate ($Na_3PO_4 . 12H_2O$) in 100 c.c. of distilled water and pour the solution on 10 gm. of gelatin. Allow the latter to swell for three to four hours, then disperse on the water bath at 100° C. and filter at 80° to 90°. Even the best brands of gelatin give a precipitate with the phosphate, but the procedure prescribed makes it coarser than it would be if the sodium salt were added to the sol. Test tubes, ½″ or ⅝″ diameter, are filled with the filtered sol to about two-thirds and allowed to cool slowly. The sol must be poured slowly *down the side of the test tube*, to avoid the formation of froth or bubbles. After the tubes have stood for at least one hour, any of the following solutions may be poured on, all of which give numerous excellent stratifications : 10 per cent. $CaCl_2$ ; a mixture of two parts of 10 per cent. $CaCl_2$ and three parts of 10 per cent. NaCl solution ; 20 per cent. crystallized calcium nitrate ($Ca(NO_3)_2 . 4H_2O$). Formation of strata continues down to the bottom of the tube and is complete in seven to ten days.

*Lead Iodide in Agar.*—Dissolve 4 gm. of potassium iodide in 100 c.c. of 1 per cent. agar sol, prepared and filtered as described above. Pour the sol into test tubes exactly as explained in the preceding paragraph and allow them to cool slowly. When they have reached the room temperature, pour on a 30 per cent. solution of crystallized lead nitrate ($Pb(NO_3)_2$). The reaction proceeds rather rapidly, and the first, very fine, strata will generally be visible in the course of one hour.

*Lead Chromate in Agar.*—For this experiment the agar has to be carefully purified in the following manner: Place 1 gm. of shred agar in a *weighed* 200-c.c. beaker and soak it in three changes of distilled water, allowing eight hours or thereabouts for each change. After the last lot has been poured off, the total weight of water (a good deal has been imbibed by the agar) is made up to 100 gm. (*i.e.*, the total weight to 101 gm. + weight of beaker), the agar is dispersed on the boiling water bath and 0·1 gm. of crystallized lead acetate ($PbA'_2 . 3H_2O$) dissolved in it. The sol is strained through a plug of glass wool and filled into test tubes as before. After cooling, a solution of 0·5 gm. of potassium dichromate in 100 c.c. of water is poured on. The stratifications, owing to the low concentrations, are very delicate, but exceedingly numerous and regular. They form throughout the length of the test tube and, as the dichromate is in large excess, the gel is coloured a faint yellow.

As agar does not adhere to glass, trouble is occasionally caused by the aqueous solution creeping between the glass and the gel. This may be prevented in the following manner: a sol containing 10 gm. of gelatin and 3 gm. of potassium dichromate in 100 c.c. of water is prepared. The test tubes to be used are filled with the sol, emptied with constant turning round their axis, so that a uniform coating of gelatin is left, and allowed to cool with their open ends downwards. They are then *exposed to direct sunlight or full daylight* for several hours, during which time the gelatin coating dries and becomes insoluble. Finally they are filled with water, which is changed until it remains quite colourless, emptied and dried. Agar adheres perfectly to the tanned gelatin surface obtained in this fashion.

Many other reactions may be studied in eithe gelatin or agar gels, particulars of which will b

found in the literature. The following points should generally be remembered. If the aqueous solution is to diffuse into the gel at all, its *molecular* concentration must be in excess (generally considerable) of that in the gel. The concentration need not, however, be exclusively due to the reacting solute, but may be partly made up by an inert salt. Thus in the tricalcium phosphate reaction, solutions of calcium chloride alone, or mixtures of calcium and sodium chloride, give good results; in the latter the concentration of $CaCl_2$ is lower, but *the total molar concentration*, $CaCl_2 + NaCl$, is as high, or higher, as with $CaCl_2$ alone. This particular expedient always deserves trial when solutions at reasonable concentrations do not give good results, or when salts of low solubility have to be tried, which do not diffuse into the gel with sufficient rapidity at the highest attainable concentrations. Differences in the qualities of the gelatin used, and in the procedure adopted in preparing the gels, may affect the results profoundly; this is particularly the case when the salt dissolved in the gelatin is not neutral in the concentrations employed, *e.g.*, $Na_3PO_4$. Agar is less variable and is also much less affected by many substances which attack gelatin, such as acid or alkali liberated by hydrolysis, so that it is to be preferred when possible. A reaction which gives good results in gelatin, however, generally does not do so in agar, and *vice versâ*; thus Liesegang's reaction does not lead to good stratifications in agar, while the lead iodide reaction does not produce them in gelatin.

It is nevertheless sometimes possible to obtain stratifications with a combination that does not produce them directly, by the intermediate formation of a reaction product which appears in that form. Two examples may be tried as follows:—

*Liesegang's Silver Chloride Rings.*—Disperse 2 gm. of gelatin in 20 c.c. of water and add 1 c.c. of 20 per

cent. solution of $AgNO_3$. Cover a glass plate, about 5″ × 7″, with the sol and allow it to set. Then place on it, in the manner described for the silver chromate experiment, a large drop of 20 per cent. solution of NaCl. The latter diffuses into the gel and forms AgCl, which is deposited as a continuous zone. If, however, a few small grains of silver chromate (*i.e.*, the precipitate of varying composition obtained by mixing solutions of dichromate and silver nitrate) are placed at points about 10 to 15 mm. from the edge of the original drop, *rings of silver chloride are formed beyond them* as the NaCl diffuses to that distance. This is, of course, due to the formation of sodium chromate and dichromate, which diffuses into the gel containing $AgNO_3$, with the formation of the usual rings, which, however, are transformed into AgCl when the solution of NaCl reaches them.

*Lead Chromate in Gelatin.*—Begin the Liesegang experiment exactly as described. When a ring of silver chromate 2 or 3 mm. wide has formed, remove the drop of silver nitrate completely with blotting paper, without spreading it, and replace it by a drop of 30 per cent. lead nitrate solution. The lead replaces the silver in the chromate formed, while the resulting $AgNO_3$ diffuses ahead, forming fresh rings, etc. *Lead nitrate placed directly on the dichromate gelatin does not form rings, but only a continuous band.*

*Reactions in Silicic Acid Gel.*—Two methods are possible. A silicic acid sol is prepared in the manner described above, and the one reaction component dissolved in it to the required concentration; the sol is then filled into test tubes and allowed to set. This method is attended with several difficulties. Some salts, *e.g.*, iodides or thiocyanates, retard the setting very considerably. Repeated heating of the sol, but not to boiling, may reduce the time required for coagulation. Other salts, such as carbonates and phosphates, promote setting to such an extent

that they frequently cannot be dissolved completely before it occurs.

The alternative method is to decompose the sodium silicate with the acid of which it is desired to form insoluble salts, and to use directly the gel thus obtained, which, of course, contains the sodium salt of the acid used. A 10 to 15 per cent. solution of crystallized sodium silicate is a suitable starting material (prepared with *boiled* distilled water and filtered, if necessary). A dilute acid is then prepared, containing in a given volume approximately the amount necessary to decompose the sodium silicate, calculated as $Na_4SiO_4$, contained in the *same volume* of silicate solution. A preliminary trial is then made by adding to a known volume of the dilute acid some methyl orange and titrating with the sodium silicate solution until the mixture is just neutral. It is then set aside and allowed to coagulate; if coagulation occurs within a reasonable time, say 12 hours, the ratio of acid to silicate may be adopted. The necessary quantities of dilute acid and sodium silicate are thoroughly mixed (of course without the addition of any indicator), and the mixture poured into test tubes and allowed to set, when the aqueous solution is poured on. The following give fine results: gel obtained by decomposition with HCl and, therefore, containing NaCl, on it 25 per cent. solution of $Pb(NO_3)_2$; gel obtained by decomposition with phosphoric acid and containing sodium phosphates, on it 20 to 30 per cent. solutions of $CuSO_4$, $BaCl_2$, $Sr(NO_3)_2$, $MnCl_2$, etc. Many other combinations will readily suggest themselves.

*Preservation of Specimens.*—The plates obtained by Liesegang's method are allowed to dry and may then be kept indefinitely in a dry place. If exposed to the atmosphere the silver chromate is, however, superficially transformed into sulphide, which shows

the colours of thin films. This may be prevented by a cover plate cemented on with Canada balsam.

The specimens in test tubes must be kept from drying and, in the case of gelatin, from putrefaction. It is advisable to harden the latter with a 2 per cent. solution of formaldehyde. The aqueous solution left in the test tube is poured off and replaced by the formaldehyde solution, which is allowed to diffuse into the gel for three or four days and is then poured off. The tubes, as well as those containing agar specimens, may then either be drawn out and sealed, or closed with corks covered with paraffin or sealing wax. If the tubes are sealed off, this must be done very slowly so as not to form a vacuum in the upper half of the tube, since this causes the formation of gas bubbles in the gel, which disfigure the preparations.

# NAME INDEX.

# SUBJECT-MATTER INDEX.